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COMBUSTION OF HETEROGENEOUS
CONDENSED SYSTEMS

(GORENIE GETEROGENNYKH
KONDENSIROVANNYKH SISTEM)

by

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Moscow, Nauka publication (1967)

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Technical editing

G. S. Pearson

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INTRODUCTION

Heterogeneous condensed systems may be regarded as mechanical mixtures of solid or viscous liquid fuels and oxidizers.

The most interesting systems of this type at the present time are the composite solid propellents (for rocket, ramjet and other engines) and pyrotechnic mixtures (for further details see Refs. 159, 222, 223 and others).

Neither of these two classes of condensed systems is new. In fact the history of the use of black powder as a rocket fuel and the history of various pyrotechnic mixtures go back many centuries. However, at the end of the nineteenth century black powder lost its significance as a rocket fuel, at first because of the temporary loss of interest in rocket technology and then, after the beginning of the rapid development of rocket technology in the twenties of our century, on account of the introduction of liquid rocket engines and motors with a solid fuel of the double-base type. Interest in pyrotechnic mixtures continues unchanged, but because of the rather limited volume of their production, investigations on the mechanisms of burning of pyrotechnic mixtures have only been carried out on a small scale. Apart from this, research in this area is much more difficult on account of the great variety in the characteristics of the components of different pyrotechnic mixtures.

It is natural, therefore, that the theory of combustion, which began to be developed about 1890, was worked out first of all for the combustion of gases, which is of great practical significance and has much simpler laws. It should also be remembered that many results obtained from the study of the kinetics of gas reactions at lower temperatures can be applied to investigations of the combustion of gases.

Later it was established that the thermal theory of combustion can be applied successfully to describe the combustion of volatile homogeneous condensed systems. For non-volatile homogeneous systems aspects of the thermal theory of combustion were applied mainly to reactions in the condensed phase. These aspects were supplemented by a series of qualitative concepts, especially concerning the expulsion of particles from the surface of a burning charge.

Interest in homogeneous condensed systems and the amount of research on them considerably increased about 1950 on account of the rapid development of composite solid rocket propellents of various types.

At the present time there are several dozen papers in the literature which deal with work on the combustion of heterogeneous systems. Qualitative concepts of the combustion of heterogeneous condensed systems and the elements of a quantitative theory can be derived from the results of this work and with the support of deductions from the thermal theory of combustion.

CHAPTER I

BASIC PROCESSES DETERMINING THE RATE OF COMBUSTION OF VARIOUS TYPES OF FLAMES

In general the rate of burning depends on the rate of mixing of the initial components in the heating zone and in the reaction zone (for heterogeneous systems), on the rate of the chemical reactions between the components, and on the rate of transfer of heat and reactive species from the reaction zone to the initial system. The normal rate of burning (and especially the form of the combustion front) depends on the flow conditions of the unburnt mixture* and of the products of combustion (especially for combustion in engines).

Naturally it is out of the question to derive a single formula for the calculation of the burning rate that is applicable to all cases or even a single system of equations of not too unwieldy character and suitable for numerical calculations.

Consequently, several basic types of flame are considered in the theory of combustion. These differ in their scientific and practical significance and in the extent to which they have been studied. The parameters of the greatest interest for a given type of flame are different; the approach to the theoretical treatment is essentially different for each type of flame; finally there are several differences in the experimental methods.

The types of flame which are the most important for the theory of combustion may be enumerated as:

(1) The laminar flame in a homogeneous gaseous mixture. The flame produced by combustion of volatile explosives belongs to this type.

(2) The laminar diffusion flame; in this case a stream of fuel gas burns in an oxidizing atmosphere. An example of this type is the flame produced during the diffusive burning of liquid fuel poured into a cylindrical vessel, etc.

(3) The flame produced during the burning of a drop of liquid fuel or of a particle of solid fuel in an oxidizing atmosphere.

(4) Turbulent flames in homogeneous or non-premixed gas mixtures.

*For gaseous systems or systems consisting of gas plus solid particles (or liquid drops).

(5) The flame produced during the burning of non-volatile explosives, powders, etc. when the reaction in the condensed phase is the most important.

There are many intermediate types, for example, the combustion of a suspension of solid fuel particles or a suspension of liquid fuel drops in a stream of gaseous oxidizer (this type has features characteristic of a flame type 3 and 1, or 3 and 4). It is these intermediate types which are of the greatest technical interest.

The combustion of condensed mixtures is also an intermediate case which combines to some extent the features characteristic of flames type 1, 2, 3 and 5. Turbulence can also play a definite role in the combustion of condensed mixtures, although in conditions completely different from those in flames of type 4.

Some characteristics of the basic types of flames may be examined briefly from the point of view of their usefulness in understanding the mechanism of combustion of condensed mixtures.

We will consider first the definition of burning rate. The concept of normal burning rate (u_n) has an important and fundamental significance in the laminar combustion of gas mixtures and homogeneous systems. By definition u_n is the velocity of displacement of the flame front relative to the unburnt mixture in a direction perpendicular to the surface of the flame at the given point. The dimensions of u_n in the Systeme Internationale are m/sec, although this unit is as yet rarely used for burning rates and then only for gaseous systems. The quantity u_n is usually expressed in cm/sec for gas systems and for condensed systems in mm/sec; if the burning rate of condensed systems were expressed in m/sec then in the usual pressure range very small fractional numbers would be obtained.

In homogeneous condensed systems, measurements are most frequently made on the burning rate of end-burning cylindrical charges, where it is assumed that the burning front is plane. It has been shown experimentally that, in the majority of cases where a coating has been applied, this assumption is correct and distortions are only observed at the edges of the charge. In addition for solid substances, and for sufficiently viscous liquid substances, the initial solid or liquid remains stationary during the period of combustion. Hence the normal burning rate is then simply the observable velocity of the flame (in the laboratory system of coordinates) and is constant at different points of the charge.

The conditions are similar when measurements are made on the burning rate of gas mixtures on a flat-flame burner, with the only difference that in this case the combustion front is stationary and the unburnt mixture moves with a velocity $v = u_n = V/S$, where V is the volumetric discharge of gas through the burner, cm^3/sec , and S is the area of cross-section of the burner, cm^2 . The analogy is even more complete in that the volatile explosives first vaporize and the stream of vapours burns in the combustion front; however, for condensed substances the burning rate is measured relative to the condensed phase and not to the gas phase.

In measurements of the burning rate of a gas mixture using a bunsen burner, the combustion front is cone shaped (Fig.1) and the area of its surface S_ϕ is considerably larger than that of the cross-section of the burner. The normal burning rate (mean) is equal to $u_n = V/S_\phi$. u_n can also be expressed in terms of v , the velocity of the gas flowing into the combustion front: $u_n = v \sin \phi$, where ϕ is the angle between the velocity vector of the gas and the combustion front.

For combustion of a gaseous mixture in tubes or spherical vessels the observed flame velocity (relative to the walls of the vessel) is not equal to the normal burning rate, since, owing to the expansion of the combustion products, the unburnt mixture in front of the combustion front moves relatively to the walls of the vessel.

Thus the measurement of the normal burning rate u_n is simplest for homogeneous condensed systems, since in this case the combustion front is plane and the initial substance is stationary (in the laboratory system of coordinates), and hence u_n is equal to the observed velocity of propagation of the flame, u (in the laboratory system of coordinates).

However, it should be emphasized that this concept of normal burning rate may not be applied to all types of flames (see below). In particular, in the case of greatest interest to us, that of condensed mixtures, the surface of the combustion front has a complicated form that is not stationary and there is little or no possibility of measuring its surface area. Therefore, for condensed mixtures, the burning rate is understood to be the observed velocity of displacement of the whole of the combustion zone (in the laboratory system of coordinates) regardless of the thickness of this zone or the surface area of the combustion front. It is only in the limiting case of sufficiently finely divided mixtures of volatile components, when combustion takes place in a similar way to the combustion of homogeneous systems, that the burning

rate is equal to the normal burning rate. As well as the linear burning rate the mass burning rate is also used where $m = \rho u$ and ρ is the density of the unburnt mixture. It is obvious that m is equal to the mass of substance burnt in unit time per unit area of combustion front (where u_n is used) or per unit area of cross-section of charge (where u is used). In the S.I. the dimensions of mass rate are $\text{kg m}^{-2} \text{sec}^{-1}$; however this unit is not yet found in the literature* and the quantity m is expressed as $\text{gm cm}^{-2} \text{sec}^{-1}$ ($\text{gm cm}^{-2} \text{sec}^{-1} = 10 \text{ kg m}^{-2} \text{sec}^{-1}$).

Both for gaseous and condensed systems the mass burning rate is used less frequently than linear burning rate. This is partly because it is the linear burning rate that is generally measured experimentally. However for comparison of the burning rates of gaseous and condensed systems only the mass burning rate is suitable. In fact, the quantity m for gas mixtures and volatile condensed substances has the same order of magnitude. On the contrary, the linear burning rate at low pressures for gas mixtures is several orders of magnitude higher than for condensed systems (in order to burn the same quantity of substance per unit time in the reaction zone, gas has to be supplied at a higher velocity than a solid or liquid substance, since these have a density considerably higher than the density of the gas).

Moreover, in condensed systems the mass burning rate depends on the pressure p with the same dependence as the linear burning rate and differing from it only by a constant factor, since the density of condensed systems in the pressure range of interest to us does not in practice depend on p . Consequently if the function $u(p)$ is approximated by the relationship $u = b p^\nu$, then the exponent ν will be the same for the linear and mass burning rate.

However, for gas systems where the density is proportional to the pressure, the exponent ν for the mass burning rate will be higher by unity than for the linear burning rate. Therefore to enable comparison to be made of results for gaseous and condensed systems, the mass burning rate will be used for both types of system^φ.

*We should note that if the linear burning rate is taken in mm sec^{-1} and the density in gm cm^{-3} , then for the mass burning rate we obtain the value corresponding to S.I. units

$$1 \text{ mm sec}^{-1} \text{ gm cm}^{-3} = 10^{-3} \text{ msec}^{-1} 10^{-3} \text{ kg } 10^6 \text{ m}^{-3} = 1 \text{ kg m}^{-2} \text{ sec}^{-1}.$$

^φUsually the composition of gas mixtures is expressed by percentage volume. Thus the densities of gas mixtures are readily calculated by the formula

$$\rho_{\text{mix}} = (p/R\theta) \sum_i \theta_i \mu_i$$

where $\theta_i = V_i / \sum_i V_i$, the fraction by volume of the i th gas component, and μ_i is the molecular weight of the i th gas component.

1 LAMINAR FLAME IN HOMOGENEOUS GAS MIXTURES

This type of flame has been studied in considerably more detail and more thoroughly than any other type of flame.

The flame in a homogeneous mixture (laminar and turbulent) is of considerable practical interest in connection with problems of safety in coal-mines and also of the use of every kind of storage tank or tanker containing fuel gas or a volatile liquid. In addition the investigation of several types of burners, etc. has been associated with this research.

The laminar flame in homogeneous mixtures is of exceptionally great significance in the theory of combustion, since for this type of flame the influence of chemical factors is not obscured by the mixing processes of the initial components, and the velocity profile of the unburnt mixture can be very simple.

Several different forms of a laminar, homogeneous flame have been investigated. Usually different types of burners are used. A bunsen burner flame is shown in Fig.1 and the flame of a flat-flame burner is shown in Fig.2. In these cases the flame is stationary with respect to the laboratory coordinates which renders it convenient for measurement of not only the burning rate, but the temperature and concentration profiles (by means of optical methods, thermocouples, gas sampling, etc).

The propagation of flames is also investigated in tubes and spherical vessels with rigid walls (constant volume bombs) or with elastic walls (constant pressure bombs). In these cases both the combustion front and the unburnt mixture move with respect to the laboratory system of coordinates and therefore it becomes very difficult to measure the temperature and concentration profiles. However these methods offer considerable advantages when measuring the velocity of a flame at high pressures.

The available data in the literature on the burning rate of gas mixtures will now be examined. Only the normal burning velocity will be used, but for the sake of brevity u , u_{\max} , α_{\max} , etc. will be written instead of u_n , $(u_n)_{\max}$, $\alpha_{(u_n)_{\max}}$, etc. Part of the experimental results (of Refs.2, 3, 6 and others) has been taken from the graphs. We have also calculated the values of the exponent ν in the formula $m = bp^\nu$ and the value of the temperature coefficient $\beta_m = d \ln m / dT_0$ from the experimental data given in the works cited.

A ABSOLUTE MAGNITUDE OF BURNING RATE

Let us quote first of all data on maximum burning rates and burning rates of stoichiometric mixtures (for the overwhelming majority of gas mixtures $(u_n)_{\max}$ and m_{\max} are obtained for a mixture composition not far from stoichiometric, see below).

The basic part of the experimental results refers to mixtures with air at atmospheric pressure. In this case, according to the data reviewed in Ref.1, the value of m_{\max} lies within the limits 0.03 to 0.06 gm cm⁻² sec⁻¹ for the majority (45 out of 60) of fuel gases studied. m_{\max} reaches a value of 0.1-0.2 gm cm⁻² sec⁻¹ only for hydrogen and low-molecular weight unsaturated and cyclic compounds (Table 1).

TABLE 1

Maximum mass burning rates, mass burning rates of stoichiometric mixtures and combustion temperature of stoichiometric gas mixtures at atmospheric pressure and room temperature

Fuel gas	m_{\max} , gm cm ⁻² sec ⁻¹		m , gm cm ⁻² sec ⁻¹ ($\alpha = 1$)		Calculated combustion temperature, °K	
	Mixtures with air	Mixtures with oxygen	Mixtures with air	Mixtures with oxygen	Mixtures with air ($\alpha = 1$)	Mixtures with oxygen ($\alpha = 1$)
Hydrogen	0.198 [1]	0.385 [8]	0.148 [10]	-	2345 [10] 2370 [11]	3050 [11]
Acetylene	0.186 [1]	-	0.165 [4] 0.173 [10]	1.16 [9]	2580 [10] 2520 [11]	3320 [11]
Ethylene oxide	0.113 [1]	-	0.112 [10]	-	2425 [10]	-
Ethylene	0.088 [1]	-	0.072 [4] 0.089 [10]	0.761 [4] 0.645 [9]	2340 [10]	3170 [12]
Carbon monoxide	0.0616 [1] 0.051 [2] 0.055 [8]	0.125 [2] 0.135 [8]	0.037 [8]	0.135 [8]	2570 [8]	2970 [11]
Benzene	0.06 [1]	0.46 [3]	0.06 [10]	0.46 [3]	2340 [10]	-
Propane	0.057 [1]	-	0.041 [4] 0.054 [10]	-	2260 [10]	-
Methane	0.052 [1] 0.038 [2] 0.0347 [5] 0.0435 [6] 0.0425 [7]	0.512 [2] 0.367 [8]	0.0377 [4] 0.045 [10]	0.415 [4]	2200 [10] 2220 [8]	-

The influence of the structure of the fuel molecule on the burning rate for low-molecular hydrocarbons with a straight chain has been elucidated¹³. In this case the burning rate increases with the degree of unsaturation of the bonds in the molecule (the burning rate increases in the order alkanes < alkenes < alkadienes < alkynes (Fig.3)). This effect decreases with increase in the length of chain (Fig.4), but nevertheless the burning rate of mixtures with air is approximately 25% higher for n-hexyne than for n-hexane.

There are much less data for mixtures with oxygen (at 1 atm). The burning rate of such mixtures is considerably higher than for mixtures with air (for hydrogen and carbon monoxide 2-3 times and for methane more than an order of magnitude; see Table 1). The mass burning rate of the oxygen mixtures studied lies within the limits $0.4-1.2 \text{ gm cm}^{-2} \text{ sec}^{-1}$ (except for the mixture $\text{CO} + \text{O}_2$ for which $m_{\text{max}} \approx 0.125 \text{ gm cm}^{-2} \text{ sec}^{-1}$).

Data for flames with oxides of nitrogen are also of interest (see Table 2).

TABLE 2

Mass rate of burning of homogeneous gas mixtures ($\alpha = 1$) based on oxides of nitrogen at atmospheric pressure and room temperature

Fuel	Oxidizer				
	N_2O [9]	NO [9]	NO_2 [9]	O_2	Air
H_2	0.382	0.02	0.108	0.575 [4]	0.148 [10]
C_2H_2	0.273	0.106	0.226	1.16 [9]	0.173 [10]
C_2H_4	0.208	0.073	0.079	0.645 [9]	0.089 [10]
C_2H_6	0.155	0.029	0.035	0.394 [9]	0.053 [1]

$p = 1 \text{ atm abs.}$

From Table 2 it can be seen that the burning rate for mixtures with NO is considerably lower than for mixtures with air, not to mention mixtures with oxygen. For mixtures with NO_2 the burning rate is close to the burning rate of mixtures with air. Finally the burning rate of mixtures with nitrous oxide occupies an intermediate position between the burning rates of mixtures with oxygen and with air, but is nearer to the latter.

The combustion temperatures for mixtures of hydrogen with these oxidizers are given in Refs. 11, 12 (Table 3).

From Table 3 it can be seen that the burning rate of a mixture of $H_2 + NO$ is at least an order of magnitude lower than the rate which should be observed for this mixture if the burning rate varied directly with combustion temperature.

It should be noted that two combustion zones are usually observed¹² for flames of mixtures with NO_2 . In the first zone NO_2 decomposes into $NO + 0.5 O_2$ and the oxygen reacts with the fuel. In the second high-temperature zone NO reacts with the fuel. Two reaction zones are observed in several instances also for carbon monoxide - NO flames. In this case in the first zone the decomposition of NO (with the subsequent reaction between oxygen and carbon) occurs as a result of reaction with the radicals CH , CN , NH , etc. In the second zone, where the temperature is higher, the thermal decomposition of NO becomes possible.

TABLE 3

Velocity and temperature of combustion of stoichiometric mixtures of hydrogen with various oxidizers at atmospheric pressures

	Oxidizer			
	N_2O	NO	O_2	Air
$m, \text{ gm} \cdot \text{cm}^{-2} \text{ sec}^{-1}$	0.382 [9]	0.02 [9]	0.575 [4]	0.148 [10]
T_c (calculated), $^{\circ}K$	2960 [11]	3110 [12]	3050 [11]	2345 [10] 2370 [11]

Some results can be given for the decomposition flames of endothermic compounds (in the gas phase at atmospheric pressure): ozone¹⁴ ($T_o = 27^{\circ}C$); hydrazine¹⁵ ($T_o = 150^{\circ}C$); ethylene oxide¹⁶ ($T_o = 25^{\circ}C$) and acetylene¹⁸ (at 2 atm abs):

	O_3	N_2H_4	$(CH_2)_2O$	C_2H_2
$m, \text{ gm cm}^{-2} \text{ sec}^{-1}$	0.928	0.17	0.0049 ^b	0.0061
T_c (calculated), $^{\circ}\text{K}$	2677	1950	1217	2560 ^b

^b In Ref. 17, $m = 0.0225 \text{ gm cm}^{-2} \text{ sec}^{-1}$ was obtained.

^b Without taking into account the loss in radiation by carbon particles.

TABLE 4

Maximum rates of burning of gas mixtures at high pressures

Mixture	$m_{\text{max}}, \text{ gm cm}^{-2} \text{ sec}^{-1}$					
	5 atm	10 atm	20 atm	40 atm	60 atm	90 atm
H_2-O_2	4.5 [4]*	-	-	-	-	211 [2]
CH_4-O_2 [2]	-	-	15.5	-	-	67.3
$CO-O_2$ [2]	0.70	-	4.18	-	10.6	15.3
H_2-NO [2]	0.23	-	1.29	-	-	-
C_2H_2 - air [4]*	0.88	1.74	-	-	-	-
C_2H_4 - air [4]*	0.32	0.60	1.02	-	-	-
CO - air [2]	-	-	0.79	-	-	1.82
CH_4 - air	0.13 [4]*	0.20 [4]*	0.24 [2]	0.26 [5]	0.29 [5]	0.51 [2]
	0.11 [6]	0.14 [5]	0.29 [4]*	0.25 [7]	-	-
	0.11 [7]	-	0.21 [7]	-	-	-
C_2H_2 - decomposition	0.08 [19]	0.094 [18]	-	-	-	-
C_3H_4 - decomposition [18]	-	0.033	0.07	0.146	-	-

* $m_{\alpha=1}$ is given instead of m_{max} .

At high pressures the data are sparse and only methane-air mixtures have been studied relatively thoroughly (Table 4). It should be noted that at high pressures the difference between the rates of burning of mixtures with oxygen and air mixtures is even more marked.

B DEPENDENCE OF BURNING RATE ON THE OXIDIZER/FUEL RATIO

The mixture composition at which the burning rate is a maximum is now considered, as is the effect on the burning rate of changes from this composition. The oxidizer fuel ratio may be conveniently defined by the coefficient

$$\begin{aligned}\alpha &= (\xi_{ox}/\xi_f)/(\xi_{ox}/\xi_f)_{stoich} \\ &= (\vartheta_{ox}/\vartheta_f)/(\vartheta_{ox}/\vartheta_f)_{stoich}\end{aligned}$$

where ξ_{ox} , ξ_f and ϑ_{ox} , ϑ_f are the fractions, by weight and by volume, respectively, of oxidizer and fuel in the given mixture; $(\xi_{ox})_{stoich}$, $(\xi_f)_{stoich}$, $(\vartheta_{ox})_{stoich}$ and $(\vartheta_f)_{stoich}$ are the same quantities in a stoichiometric mixture⁶. Correspondingly, for excess fuel $0 < \alpha < 1$, for a stoichiometric mixture $\alpha = 1$, and for excess oxidizer $1 < \alpha < \infty$.

⁶For calculating the stoichiometric composition in mixtures of gases, in which the 'fuel' consists of one or several fuel gases (with fractions by volume ϑ'_{fi} in relation to the 'fuel'), and the 'oxidizer' consists of an active gas, e.g. O_2 , and inert diluents, e.g. N_2 , with fractions by volume ϑ'_{ox} , ϑ'_{in} (in relation to the 'oxidizer'), one can use the formula

$$(\vartheta_f)_{stoich} = \left[1 + \left(\sum_i k_i \vartheta'_{fi} \right) / \vartheta'_{ox} \right]^{-1} \quad (1)$$

in which k_i is the number of moles of the oxidizer necessary for the complete oxidation of one mole of the i th fuel component.

Thus, for example, for hydrogen-air mixtures, $k_{H_2} = 0.5$, $\vartheta'_{H_2} = 1$ (hydrogen without additive), $\vartheta'_{ox} = 0.295$. If in the composition of the fuel there is an inert gas, then for it $k_i = 0$. If the oxidizer consists only of an active component, then $\vartheta'_{ox} = 1$. Correspondingly, for mixtures of fuel gas (without additive)/ O_2 , formula (1) simplifies to

$$(\vartheta_f)_{stoich} = (1 + k_i)^{-1} \quad (1)$$

It may be noted when considering the position of the maximum burning rate it is possible in practice to obtain the same result using either the mass or the linear burning rate, since the density of the majority of gases and condensed mixtures changes relatively little over a reasonably wide range of α . The only exceptions to this are mixtures consisting of components of widely differing densities such as H_2-O_2 or $W-KClO_4$, where m_{max} can be perceptibly displaced in relation to u_{max} towards the greater percentage of the heavy component.

The position of the maximum burning rate of gas mixtures is now examined.

For mixtures with air ($p = 1$ atm abs), the data reviewed in Ref. 1 have u_{max} close to $\alpha = 1$; for some mixtures it is obtained with a small excess of fuel ($\alpha > 0.8$), for others with a small excess of oxidizer ($\alpha < 1.12$). Exceptions are mixtures of CO-air and H_2 -air, where u_{max} is found for considerably fuel-rich mixtures, for example, with CO-air mixtures at $\alpha \approx 0.49$.

By reduction in the dilution of a mixture by an inert component and, in particular, in the transition from air to oxygen mixtures, the maximum burning rate of H_2 and of CO mixtures is displaced towards the stoichiometric. Thus, for example, Yang (cited in Ref. 8) found that, for a change of oxygen content in the composition of the oxidizer $x\% O_2 + (100 - x)\% N_2$ from $x = 21\%$ to $x = 98.5\%$, the maximum burning rate for hydrogen is displaced from $\alpha = 0.56$ to $\alpha = 0.78$, and for carbon monoxide from $\alpha = 0.37$ to $\alpha = 0.62$. For benzene³, a change of x from 16.4 to 88.6% displaced the maximum burning rate from $\alpha = 0.74$ to $\alpha = 0.92$. However, with methane (according to Yang's data) a significant shift of the maximum is not observed for a change of x from 21 to 98.5%.

There are only a few works^{2,5,7} in which the relationship $u(\alpha)$ at high pressures has been studied. The position of u_{max} was established with reasonable accuracy (e.g. in Refs. 5 and 7 the interval of α near u_{max} consisted of $\Delta\alpha \approx 0.1$). On considering the quoted accuracy of determination of the position of the maximum in the work^{2,5,7}, the conclusion may be reached that increase of pressure does not lead to a significant displacement of u_{max} . Only for CO is there a marked² displacement of u_{max} towards stoichiometric with increase of pressure (Table 5).

TABLE 5

Displacement of maximum burning rate with increase of pressure for CO mixtures

Pressure, atm abs	$\alpha_{u_{max}}$		Pressure, atm abs	$\alpha_{u_{max}}$	
	CO-O ₂	CO-air		CO-O ₂	CO-air
1	0.60	0.40	52	0.82	-
5.1	0.70	-	90	0.86	0.71
21.4	0.82	0.53			

Thus, for gaseous mixtures when they are not excessively diluted by inert components and the pressure is sufficiently high the maximum burning rate lies close to the stoichiometric composition.

As the composition of the mixture is changed from $\alpha_{u_{max}}$ (i.e. that composition associated with maximum burning rate), the curve $u(\alpha)$ initially falls rather gently, and then very steeply, and finally at some α_{crit} combustion ceases. We shall characterize the form of the curve $u(\alpha)$ by the ratio u/u_{max} at various values of $\alpha/\alpha_{u_{max}}$.

We may note two results obtained from gaseous mixtures.

(1) Reduction of the amount of inert diluent and, in particular, on transition from air to oxygen causes the curves $u(\alpha)$ to become less steep^{2,3}. In other words excess of fuel or oxidizer in the mixture with oxygen is less strongly reflected in the burning rate, than in mixtures with air (Table 6).

TABLE 6

Reduction of the burning rate of mixtures of benzene + x% O₂ + (100 - x)% N₂
 with departure of mixture composition from $\alpha_{u_{\max}}$ at
 various percentages of nitrogen³ ($p_e = 1$ atm)

$\alpha/\alpha_{u_{\max}}$	u/u_{\max}						
	x = 20.8	x = 28.4	x = 40.0	x = 51.5	x = 67.2	x = 83.3	x = 100
1.6	-	-	-	0.87	0.92	0.89	0.94
0.8	0.85	0.91	-	0.96	0.97	0.98	0.95
0.7	0.66	0.77	0.80	0.87	0.89	0.93	0.88
0.6	0.48	0.56	0.61	0.69	0.73	0.77	0.74
0.5	0.28	-	0.40	0.42	0.49	-	0.47

(2) The quantity u/u_{\max} can vary significantly with pressure². For CO-O₂, CO-air and CH₄-O₂ mixtures at a value of α , sufficiently far from $\alpha_{u_{\max}}$, a substantial reduction of u/u_{\max} is observed with increase of pressure. In other words, excess of a component reduces the burning rate more at high pressures than at low pressures (Table 7).

TABLE 7

Reduction of the burning rate of gaseous mixtures with change of the
 mixture composition from $\alpha_{u_{\max}}$ at various pressures²

Mixture	$\alpha/\alpha_{u_{\max}}$	u/u_{\max}				
		p = 1 atm	p = 5.1 atm	p = 21.4 atm	p = 52 atm	p = 90 atm
CO-O ₂	3.0	0.74	0.67	0.50	-	-
	2.5	0.80	0.76	0.61	-	-
	0.5	0.84	-	0.61	0.63	-
	0.4	0.77	-	0.42	0.42	-
CO-air	1.6	0.86	-	0.74	-	0.51
	1.4	0.92	-	0.84	-	0.70
CH ₄ -O ₂	1.6	0.82	-	0.78	-	0.73
	0.6	0.72	-	0.32	-	0.41
	0.5	0.52	-	0.13	-	-

C DEPENDENCE OF BURNING RATE ON PRESSURE

We may approximate to the actual curve of $m(p)$ by a function

$$m = b p^{\nu} . \quad (2)$$

If the pressure range is wide, then the curve must be divided into several sections, and the values of b and ν determined separately for each section. Nevertheless the application of equation (2) is justifiable on account of its simplicity and convenience.

For all the oxidizing mixtures studied, which are rather few, the value of ν lies close to unity (Table 8) and does not display a systematic dependence on α . For H_2-O_2 mixtures the exponent ν is appreciably greater than unity²: in the pressure range 14 to 90 atm $\nu_{(\alpha=1.33)} = 1.42$, $\nu_{(\alpha=0.86)} = 1.56$.

For mixtures with air the value of ν is generally lower than for those with oxygen. For methane-air $\nu \approx 0.5$, although individual values show a sharp drop (see Table 8). For mixtures of propane, ethane and ethylene with air⁶ the value of ν is appreciably greater ($\nu \approx 0.65 - 0.85$), and for C_2H_2 -air mixtures⁴ $\nu \approx 1$.

In a number of cases the exponent ν depends significantly on pressure. Also for some mixtures the value of ν falls at very high pressure (see Table 8, data for CH_4 -air with $\alpha = 1.2$ and 0.90 , and also data for CO-air). On the other hand, for other mixtures the value of ν increases at high pressures (see Table 8, data for CH_4-O_2 with $\alpha = 0.75$ and 0.61).

For CO-air a reduction of ν is observed for an increased excess of fuel (particularly at high pressures, see Table 8). High values of ν are obtained for the decomposition flames of acetylene ($\nu_{4-10 \text{ atm}} \approx 1.44$ ¹⁸; $\nu_{2.5-5 \text{ atm}} \approx 2.1$ ¹⁹) and propyne ($\nu_{10-40 \text{ atm}} \approx 1.06$ ¹⁸).

TABLE 8
The value of the exponent ν in the formula $m = b p^\nu$ for various gas mixtures
(pressure in atm shown by figures in curved brackets)

Mixture	α	2.0	1.5	1.16	0.93	0.75	0.61
$\text{CH}_4\text{-O}_2$ [2]	ν	1.04 (1-90)	1.07 (1-90)	1.13 (1-90)	1.13 (1-90)	1.08 (1-21) 1.25 (21-90)	0.98 (1-21) 1.29 (21-90)
	α	3.0	2.0	1.33	0.86	0.5	
$\text{CH}_4\text{-air}$	ν	1.06 (5-21)	1.15 (5-52)	1.10 (1-90)	1.08 (1-90)	1.04 (1-90)	
	α	1.2	1.1	1.0	0.95	0.90	0.80
CO-air [2]	ν	0.70 (1-21) 0.54 (1-60) 0.37 (21-90)	0.44 (2-19) [7]	0.68 (1-20) [4] 0.48 (2-40) [7]	0.59 (1-21) [2] 0.52 (1-60) [5]	0.48 (2-19) [7] 0.53 (1-60) [5] 0.23 (19-40) [7]	0.22 (2-40) [7]
	α	0.98	0.78	0.63	0.51	0.42	0.34
CO-air [2]	ν	0.90 (1-21) 0.74 (21-90)	0.92 (1-21) 0.74 (21-90)	0.91 (1-21) 0.66 (21-90)	0.92 (1-21) 0.46 (21-90)	0.84 (1-21) 0.34 (21-90)	0.73 (1-21) 0.11 (21-90)

D DEPENDENCE OF BURNING RATE ON INITIAL TEMPERATURE

An increase of the initial temperature T_0 increases the mass (and especially the linear) burning rate (Fig.5).

The data of Passauer (quoted in Ref.8) are satisfactorily described by the empirical formula

$$m = b' T_0 \quad (3)$$

where T_0 is expressed in $^{\circ}\text{K}$.

Then if the dependence of burning velocity on flame temperature T_c is expressed by

$$m \approx e^{-E/2RT_c} \quad (4)$$

where E is the activation energy, cal mole^{-1} , then in the absence of dissociation the dependence $m(T_0)$ will have the form

$$m \approx e^{-E/2R(T_0 + q/\bar{c})}, \quad (4')$$

where q is the heat of combustion, cal gm^{-1} , and \bar{c} is the average specific heat of the reaction products, $\text{cal gm}^{-1} \text{ deg}^{-1}$.

The dependence $u(T_0)$ is also characterized by the ratio $u_{T_{01}}/u_{T_{02}}$ of the burning rates for definite initial temperatures (for example $u_{100^{\circ}}/u_{200^{\circ}}$) or by the coefficient

$$\beta_u = \frac{1}{u} \frac{\partial u}{\partial T_0} = \frac{\partial \ln u}{\partial T_0} \quad (5)$$

or by the analogous coefficient for the mass burning rate

$$\beta_m = \frac{1}{m} \frac{\partial m}{\partial T_0} = \frac{\partial \ln m}{\partial T_0} \quad (6)$$

For condensed systems β_u and β_m are similar to each other since the dependence of density on the initial temperature is slight and in many cases it may be ignored. For gas systems

$$m = \rho_g u = \frac{p\mu}{RT_0} u = \frac{p\mu}{R} \cdot \frac{u}{T_0},$$

where μ is the molecular weight.

For $p = \text{constant}$ we obtain in place of (6)

$$\beta_m = \frac{\partial \ln u/T_0}{\partial T_0} \quad (6')$$

It is obvious that the coefficients β_u and β_m are themselves dependent on the initial temperature. Thus if there is a dependence $m(T_0)$ of type (3), then $\beta_m = 1/T_0$ (for example at room temperature $\beta_m \approx 3.4 \cdot 10^{-3} \text{ deg}^{-1}$ and at 500°C $\beta_m \approx 1.3 \cdot 10^{-3} \text{ deg}^{-1}$). If then (4') is true, then

$$\beta_m = E/2RT_0^2 = E/2R(T_0 + q/c)^2 \quad (7)$$

But if the change in T_0 is not too large, the experimental points in the coordinates $(\ln m, T_0)$ or $(\ln u/T_0, T_0)$ lie satisfactorily on a straight line in many cases which gives the mean value β_m for the given change in T_0 . Values of β_m determined in this way for a series of mixtures of gases at atmospheric pressure are given in Table 9.

From Table 9 it may be seen that for stoichiometric mixtures of H_2 , CH_4 , C_3H_8 , C_6H_6 , $n\text{-C}_7\text{H}_{16}$, $\text{iso-C}_8\text{H}_{18}$ in air the values of β_m are close to $2 \cdot 10^{-3} \text{ deg}^{-1}$ and differ little. We may also note that the flame temperatures of stoichiometric mixtures of H_2 , CH_4 , C_3H_8 , C_6H_6 vary only slightly and are close to $2200\text{--}2300^\circ\text{K}$ (see Table 1).

If we calculate the value of the activation energy from (7) we obtain for $\alpha = 1$

Fuel gas (+ air)	H_2	CH_4	C_6H_6
E , kcal/mole	44	38.5	34.8

TABLE 9

Value of the temperature coefficient of burning rate $\beta_m = \frac{\partial \ln m}{\partial T_o}$

for a series of air mixtures at atmospheric pressure

α	$\beta_m \cdot 10^3$					
	Passauer's data ⁸		Data of Ref. 21	Data of Ref. 22		
	Hydrogen*	Methane	Propane ⁶	Benzene	n-pentane	iso-octane
1.43			2.09 (38-538°C)			
1.18		2.46 ^h (20-520°C)				
1.11			1.70 (38-538°C)	1.64 (25-427°C)		1.74 (25-434°C)
1.05		2.08 ^h (20-520°C)				
1.0	2.01 (20-430°C)			1.60 (25-427°C)	1.78 (35-306°C)	1.53 (146-434°C)
0.94		1.90 ^h (20-520°C)				
0.91			1.51 (38-538°C)	1.72 (25-427°C)	1.69 (35-306°C)	1.65 (25-434°C)
0.88		1.62 [5] (16-220°C)				
0.86		1.90 ^h (95-520°C)				
0.79		3.76 (95-350°C) 0.96 (350-680°C)				
0.77			1.56 (38-538°C)			
0.74	1.99 (190-430°C)	1.07 (350-610°C)				
0.68		2.13 (350-520°C)	1.90 (38-538°C)			

*For $\alpha = 1.48$; 0.59; 0.49 and 0.42 the value β_m continuously decreases with the increase of T_o .

⁶For $\alpha = 0.59$ the value β_m continuously decreases with the increase of T_o in the interval 205-538°C.

^hFor the interval 520-680°C β_m decreases.

As the initial temperature increases β_m decreases in agreement with (7) or with the dependence $\beta \approx 1/T$ (which follows from (3)). This is especially noticeable for rich mixtures.

Finally, for the mixtures given in Table 9, the effect first observed by G.V. Lukashenya is particularly clear: for a change of α , i.e. a change of the mixture composition, the temperature coefficient β_m goes through a minimum close to where the maximum burning rate is found (Fig.6).

E INFLUENCE OF SMALL ADDITIONS ON THE BURNING RATE

Several investigators have shown experimentally that small additions of gas or of finely divided solid particles can influence the burning rate of homogeneous gas mixtures to a considerable extent.

The burning of carbon monoxide is the best known example.

Carefully dried CO-O₂ mixtures generally do not ignite. But on addition of small quantities of water vapour which reduces the calculated heat of combustion the mixture becomes flammable, and the rate of burning increases as the percentage of water increases up to a limiting value. The data obtained by Bone²³ for mixtures of 45% CO + 55% air were:

water vapour, %	0.7	1.45	3.5	5.2	80
u, cm/sec	58	76	106	120	118

In Ref.24 the action of a large number of gaseous additives on the burning rate of mixtures of H₂-air was investigated. In Table 10 are presented the data obtained for the burning rate and also for the value $Z = u_a/u_p$ where u_p is the burning rate of the original mixture, and u_a the burning rate of the mixture with additives.

TABLE 10

The effect of various gaseous additives on the burning rate
of mixtures of H_2 -air at $\alpha \approx 0.7$

Content of additive 2% by volume; $p = 1$ atm abs; $T_0 = 25^\circ C$

Additive	u , cm/sec	Z	Additive	u , cm/sec	Z
Without additive	300	-	1.1 Difluorethane	135	0.45
1.3 Butadiene	27	0.09	Methane	144	0.48
n-Butane	46	0.15	Methyl bromide	154	0.51
Dibromotetrafluoroethane	54	0.18	Methyl chloride	199	0.66
Ethyl chloride	80	0.27	1.1 Difluorethylene	202	0.67
Ethylene	100	0.33	Vinyl chloride	230	0.77

Besides the compounds listed in Table 10, additions of acetylene and ammonia lowered the burning rate quite effectively. On the other hand additions of SO_2 , SF_6 , NO , HCl , SiF_4 , CO_2 , BF_3 , CO , NO_2 , AlF_3 , N_2O , and Cl_2 lowered the rate insignificantly.

Vapours of some liquids such as aniline, benzene, ethyl ether, iron pentachloride, toluene, n-octane and acetone effectively lowered the burning rate; whereas acetic acid, nitromethane, tetraethyl lead, chloroform and carbon tetrachloride lowered the burning rate insignificantly. Water vapour increased the burning rate.

The reduction of the burning rate of a stoichiometric mixture of methane and air with the addition of some finely ground salts was investigated in Ref.25 (Table 11). It was noted that the effect of the additive $NaHCO_3$ on C_3H_8 -air and especially on NH_3 - O_2 - N_2 mixtures is much less than on a CH_4 -air mixture.

TABLE 11

Effect of the addition of certain powders on the burning rate
of the mixture CH_4 -air at $\alpha = 1$ at atmospheric pressure

Additive	Specific surface of mixture, cm^2/gm	Concentration of mixture, mg/cm^3	u , cm/sec	Z
Without additive	-	-	65	-
Na_2CO_3	10800	0.01	17	0.26
	4940	0.01	17	0.26
	10800	0.02	13.8	0.21
	4940	0.02	13.8	0.21
NaHCO_3	11900	0.01	19	0.29
	7760	0.01	55	0.85
	11900	0.02	14	0.22
	7760	0.02	26	0.40
	11900	0.04	13	0.20
	7760	0.04	13	0.20
KHCO_3	12400	0.01	14	0.22
NaCl	4500	0.01	31	0.48
	4500	0.02	18	0.28
CuCl	3000	0.01	34	0.52
	3000	0.02	22	0.34
	3000	0.04	15.5	0.24
K_2SO_4	5200	0.01	15	0.25

F THEORY OF PROPAGATION OF A FLAME IN HOMOGENEOUS SYSTEMS

We have already mentioned that the burning rate of homogenous systems depends on the rate of chemical reactions in the burning front, and on the rate of transfer of heat and reactive species from the burning front to the unburnt mixture.

The problem of theoretically calculating the burning rate requires the combined solution of the equations of chemical kinetics, diffusion, and heat transfer.

There have been numerous investigations which have derived either a numerical solution of the previously mentioned system of equations for the burning of a particular mixture, or an approximate solution which not infrequently yields a relatively simple expression for the burning rate of a definite class of mixtures.

In discussing these approximate theories it is usual to separate the thermal and diffusion theories.

The thermal theory of burning can be applied to cases where there are different reaction mechanisms in a flame, provided that the temperature and concentration fields are similar. The diffusion theory is applied to cases where there is a chain reaction mechanism in the flame, especially when the hydrogen atom concentration in the reaction zone is large.

The approximate thermal theory of burning is discussed briefly since for the condensed systems only a few scattered attempts²⁴⁰ have been made to apply either the approximate diffusion theory⁶ or the numerical methods of solution of the complete system of equations of burning, because of the lack of information on the reaction mechanism in the flame.

The most widely applied of the several approximate thermal theories of combustion is that developed at the end of the thirties and the beginning of the forties in the Institute of Chemical Physics of the Academy of Science of the U.S.S.R. by Ya. B. Zeldovich and D.A. Frank-Kamenetsky with the active participation of N.N. Semenov (see Refs.26, 28, 192, 193) for the burning of gases, and which was extended to the burning of volatile explosives (see Ref.46 and also 27).

In this theory it is assumed that the rate of reaction increases exponentially with temperature, and that burning proceeds in a single narrow zone in the gaseous phase⁶. In practice the heat release is concentrated over a narrow temperature range (of the order of RT_c^2/E) near to the maximum combustion temperature.

⁶Qualitative considerations of the possible effect of diffusion of the active gaseous products during the burning of ammonium perchlorate are contained in Refs.106, 107.

⁶Subject to considerable limitations, this theory can be applied also to the so-called flameless burning, where the reaction proceeds completely in a single narrow zone in the condensed phase.

In its simplest form the expression for burning rate according to this theory can be written

$$m \approx \sqrt{\frac{2\lambda \phi_{\max} RT_c^2}{q^2 E}} = \sqrt{\frac{2\lambda \phi_{\max} RT_c^2}{[\bar{c}(T_c - T_o)]^2 E}}, \quad (8)$$

where λ = coefficient of thermal conductivity of the mixture flowing into the reaction zone, $\text{cal cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$;

ϕ_{\max} = rate of heat release in unit volume of the reaction zone with $T \approx T_c$, $\text{cal cm}^{-3} \text{sec}^{-1}$;

q = heat of reaction, cal/gm ;

\bar{c} = mean specific heat, $\text{cal gm}^{-1} \text{deg}^{-1}$.

In the theory it is assumed that $\phi_{\max} \approx e^{-E/RT_c}$. The dependence of ϕ_{\max} on concentration C of the substance, and for systems reacting in the gas phase, also on pressure, is $\phi_{\max} \approx C^n$ for a simple reaction of the n th order.

Substitution in (8) yields*

$$m \approx p^{n/2} e^{-E/2RT_c} \quad (9)$$

or more fully

$$m \approx p^{n/c} \left(\frac{T_c}{T_o}\right)^{n/2} \left(\frac{RT_c^2}{E}\right)^{\frac{n+1}{2}} (T_c - T_o)^{-\frac{n+1}{2}} e^{-E/2RT_c}. \quad (10)$$

Several attempts have been made to determine the relationship between the burning rate and the combustion temperature which was varied by:

*In a number of cases the combustion temperature depends on the pressure; for example, at sufficiently high T_c , when dissociation becomes considerable, the combustion temperature increases somewhat with increase in pressure. This must be considered when analysing the dependence $m(p)$.

- (1) changing from one mixture to another;
- (2) dilution of the mixture by an inert component (for example, nitrogen) or an excess of fuel or oxidizer;
- (3) changing the initial temperature of the mixture;
- (4) removal of heat from the zone of burning by the cold burner.

For the first method a single relationship between temperature and burning rate has not been discovered, which is to be expected from (9) and (10), since the values of the activation energy can change in going from one mixture to another. Nevertheless it has been shown⁹ that for definite groups of mixtures the relationship $u(T_c)$ is the same; for example, the points for a series of hydrocarbons, alcohols and ethers in mixtures with O_2 and N_2 lie on the same curve, although this was not constructed from equations (9) and (10).

The combustion temperature has been changed by varying the initial temperature^{21,22}. The relationship $u(T_c)$ obtained was in agreement with equations (9) and (10). The values of the activation energy for mixtures of air with benzene, n-heptane and iso-octane are similar²² (Table 12).

TABLE 12

Values of activation energy for the combustion of stoichiometric mixtures in air at atmospheric pressure

Fuel gas	E, kcal/mole				Fuel gas	E, kcal/mole			
	[10]	[21]	[22]*	[29]		[10]	[21]	[22]*	[29]
Hydrogen	16	-	-	47	Propane	26	33.1	-	53
Acetylene	20	-	-	47	Benzene	27	-	43	-
Ethylene	24	-	-	50	n-Heptane	-	-	34	-
Methane	26	-	-	65	Iso-octane	-	-	39	-
Ethane	26	-	-	50					

*Results for mixtures with u_{max} .

(However $\alpha_{u_{max}}$ was 0.95 to 0.97, and thus close to $\alpha = 1$.)

The combustion temperature has also been changed owing to the removal of heat from the flame by the cold burner²⁹. In the 1300-1900°K region using coordinates $\ln u$, $1/T_c$, the experimental points fall on straight lines the slopes of which yield values of the activation energies depending only slightly on α (with the exception of the mixture CH_4 -air) and are approximately the same for mixtures of acetylene, ethane, propane and hydrogen with air.

The authors of the works mentioned emphasize that as a consequence of the complexity of the reaction mechanism in the flame the activation energy should be regarded as a composite quantity. It is not surprising, therefore, that the numerical value of the activation energy for a given mixture can depend markedly on the method of determination. In Table 12 are given the values of the activation energy calculated by starting from the function $u(T_c)$ and also the values obtained¹⁰ determined from the relationship between the activation energy and the temperature of burning at the weak limit. For the majority of fuel gases (in mixtures with air) investigated¹⁰, the value of the activation energy lies within comparatively narrow limits - from 25 to 30 kcal/mole. Appreciable divergence is observed only for carbon disulphide (16 kcal/mole), hydrogen (16 kcal/mole) and acetylene (20 kcal/mole).

The difference between the data of Ref.10 and 29 is extraordinarily great.

However, the values of activation energy in Ref.29 refer to the range of temperature 1300-1900°K. It is possible that for the adiabatic temperature (2200-2500°K for these mixtures) the value of activation energy would be lower. Evidently 30-40 kcal/mole is the usual range.

It is interesting to evaluate the order of magnitude of the rate of heat release (ϕ_{\max}) in the combustion zone. Such an evaluation is useful when comparing various types of flames, especially when investigating flames where the combustion of a homogeneous mixture and of solid particles proceeds simultaneously (see below). Unfortunately, the measurement of ϕ_{\max} (from the temperature profile) is associated with great difficulties and errors, and in practice has been achieved only at low pressures. It is possible also to evaluate the order of magnitude of ϕ_{\max} using (8) and similar relationships.

For mixtures of hydrocarbons with air some such evaluations are collected in Ref.30. At atmospheric pressure the value obtained was about $10^3 \text{ cal cm}^{-3} \text{ sec}^{-1}$. We note that the evaluation according to (8) is

$$\phi_{\max} \approx \frac{m^2 [\bar{c}(T_c - T_o)]^2}{2\lambda} \cdot \frac{E}{RT_c^2} \quad (11)$$

where $m = 0.05 \text{ gm cm}^{-2} \text{ sec}^{-1}$;

$\bar{c} = 0.3 \text{ cal gm}^{-1} \text{ deg}^{-1}$;

$T_c = 2300^\circ \text{K}$;

$T_o = 300^\circ \text{K}$;

$\lambda = 4 \times 10^{-4} \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$;

$E = 3 \times 10^4 \text{ cal mole}^{-1}$;

then $\phi_{\max} \approx 3 \times 10^3 \text{ cal cm}^{-3} \text{ sec}^{-1}$, i.e. thrice as high as in Ref.30.

For oxygen mixtures at atmospheric pressure $m = 0.1 - 0.5 \text{ gm cm}^{-2} \text{ sec}^{-1}$ (see Table 1). Taking $T_c = 3000^\circ \text{K}$ we obtain from (11) $\phi_{\max} = 1.5 \times 10^4 - 3.5 \times 10^5 \text{ cal cm}^{-3} \text{ sec}^{-1}$. Ref.12 states that the rate of consumption of oxygen in the reaction zone of a $\text{C}_2\text{H}_4\text{-O}_2$ mixture was found to be about $4 \text{ mole cm}^{-3} \text{ sec}^{-1}$, which yields a value for ϕ_{\max} of the order of $10^5 \text{ cal cm}^{-3} \text{ sec}^{-1}$.

For an increase in burning rate due to an increase in pressure ϕ_{\max} increases in proportion to the square of the burning rate (see equation (1)). Thus at a pressure of 100 atm absolute, where for mixtures of oxygen with hydrogen or methane the mass burning rate is of the order $10^2 \text{ gm cm}^{-2} \text{ sec}^{-1}$, the value of ϕ_{\max} is of the order $10^{10} \text{ cal cm}^{-3} \text{ sec}^{-1}$.

2 COMBUSTION OF VOLATILE EXPLOSIVES

The combustion of volatile explosives takes place in the gaseous phase above the surface of the charge and should therefore be subject to the same laws as the combustion of homogeneous gas mixtures.

In fact the earliest and also the most successful comparison of the approximate thermal theory of Ya. B. Zeldovich and D.A. Frank-Kamenetsky (see above) with experiment was made not for gaseous mixtures but for a volatile explosive³¹ - nitroglycol $\text{O}_2\text{NOCH}_2\text{CH}_2\text{ONO}_2$.

The absolute magnitude of the burning rate of volatile explosives and its dependence on pressure and initial temperature are similar to those for gaseous systems.

It is necessary first to emphasize the difference between the combustion of explosive materials and the combustion of gaseous systems. These differences are mainly concerned with the stability of the combustion front.

The appearance of a disturbed combustion front during the combustion of a gas mixture in a burner is connected with the occurrence of turbulence in the unburnt gas stream.

Correspondingly the condition for the stability of a laminar flame coincides with the condition for the stability of laminar flow in a tube, i.e. with the condition $Re = Rv\rho/\eta < Re_{cr}$ (where R is the radius of the tube, ρ the density of the gas and η the dynamic viscosity of the gas, $gm\ cm^{-1}\ sec^{-1}$). The presence of combustion can change only to a small extent the value of Re_{cr} (compared with flow without combustion). The results which have been collected on the theory of turbulence can be used to study the process of development of disturbances. The question of the stability of combustion of a gaseous mixture in a tube or spherical bomb is a more complicated problem. Here in particular, the effect of the self-turbulence of the plane front of the flame has also to be considered, as predicted by the theoretician L.D. Landau³². However, under usual experimental conditions this self-turbulence effect of a gas flame is apparently unable to develop.

On the other hand during the combustion of liquid explosives the self-turbulence⁶ effect can arise very easily so that laminar⁷ combustion of liquid explosives can be observed only at sufficiently low pressures.

⁶This effect was also predicted by L.D. Landau³³ and was examined in a slightly different setting by V.G. Levich⁵³. In Ref.34 some results of the theory of Landau are discussed.

⁷In the combustion of condensed systems a terminology has not yet been established to designate undisturbed and disturbed combustion. For the first are used the terms 'stationary combustion', 'stable combustion', 'normal flame propagation', 'laminar combustion' and for the second 'non-stationary combustion', 'unstable combustion', 'turbulent combustion', 'disturbed combustion', 'convective combustion' etc. To describe the transition from the first regime to the second are used the terms 'breakdown (or disruption) of the stable regime of combustion', 'transition of combustion', 'penetration of burning below surface of the charge', etc.

The burning of liquid explosives is stable³³ only at $m < m_{cr}$, where

$$m_{cr} = \left(\frac{4\alpha' g \rho_l^2 \rho_g^{\frac{1}{2}}}{\rho_l - \rho_g} \right) \quad (12)$$

Here α' is the surface tension of the liquid (at the temperature attained on the surface of the burning liquid) dyn cm^{-1} , g the acceleration of gravity cm sec^{-2} and ρ_l, ρ_g the densities of the liquid and its gaseous combustion products respectively.

The applicability of equation (12) as a criterion for the stability of combustion of liquid explosives was investigated in detail by K.K. Andreev. The values of m_{cr} calculated by him from (12) for methyl nitrate $\text{H}_3\text{C-O-NO}_2$ was $0.32 \text{ gm cm}^{-2} \text{ sec}^{-1}$ and for nitroglycol $0.88 \text{ gm cm}^{-2} \text{ sec}^{-1}$. The experimental values of m_{cr} for methyl nitrate lie between 0.26 and $0.46 \text{ gm cm}^{-2} \text{ sec}^{-1}$ (at about 1.75 atm abs) and for nitroglycol are about $0.90 \text{ gm cm}^{-2} \text{ sec}^{-1}$ (at about 20 atm)³⁵. The transition to disturbed combustion is accompanied by the strong dependence of u on p (Refs. 36, 37).

For solid explosives the disruption of laminar combustion (for a certain critical pressure p_{cr}) is connected with the appearance of gaseous products of combustion in the pores of the unburnt substance (see Refs. 35, 198, 199, 230, etc). The value of p_{cr} decreases with increase of the porosity of the charge and for a given porosity with increase in size of the crystals of the substance (since in this way the diameter of the pores increases although the number of them decreases). The presence of a liquid film on the surface of a charge produces an increase in p_{cr} . If there is the possibility of the explosive cracking in the process of combustion (under the influence of thermal stresses⁴⁰), disruption of laminar combustion can occur in those cases where the cold material was monolithic⁴³. A trivial cause of the disruption of laminar combustion can be the penetration of products into the gap (even the most insignificant amount so long as it takes place) between the charge and the coating^{38, 39}.

⁴⁰It is necessary to use a coating (or grease) because a flame can propagate along the free surface (boundary with the gas) of the charge with a velocity considerably higher than the normal rate of burning. This arises from the charge being surrounded by its gaseous combustion products^{38, 39}.

A ABSOLUTE MAGNITUDE OF BURNING RATE

The number of investigations devoted to the combustion of explosives is considerably less than for gas systems. However, whereas for gas systems almost all the data are obtained for $p < 1$ atm abs, for condensed systems almost all the investigations relate to high pressures, and some were carried out at pressures up to 1000-10000 atm. This is connected mainly with practical considerations; for ballistite powders used in gun propellents, the working pressure is of the order of 10^3 atm and for solid rocket propellents - several tens of atmospheres; and high pressures can be developed during the combustion of explosives with various coatings, etc. Apart from this, experimentally it is very much easier to work with condensed systems at high pressures than with gaseous systems.

Data are given for the burning rate of a series of explosives in Table 13.

TABLE 13

Mass burning rate of volatile explosives

Material	m, gm cm ⁻² sec ⁻¹							
	1 atm	10 atm	40 atm	100 atm	200 atm	400 atm	1000 atm	
Methyl nitrate [35] CH ₃ ONO ₂	0.143							
Nitroglycol [35] O ₂ NOCH ₂ CH ₂ ONO ₂	0.042	0.392						
Cyclonite [42] (CH ₂ NNO ₂) ₃ (PDX)	0.061**			3.06	5.22	9.54	22.5	
PETN C(CH ₂ ONO ₂) ₄			0.77 [42]	1.93 [42]	3.86 [42]	7.72 [42]	18 [44]	
Pentaerythritol tetranitrate			0.80 [201]	1.95 [201]				
Tetryl [42] * C ₆ H ₂ (NO ₂) ₃ NNO ₂ CH ₃	0.067 [35]	0.312	0.815	1.55	2.49	4.60	11.4	
Dynamite [42] * O ₂ NN(CH ₂ CH ₂ ONO ₂) ₂	0.051		0.478	1.02				
Picric acid [42] * C ₆ H ₂ (NO ₂) ₃ OH			0.46	0.945	1.75	3.36	8.19	
Trotyl [42] * C ₆ H ₂ (NO ₂) ₃ CH ₃ (TNT)			0.326	0.756	1.47	2.90	7.20 6.65 [44]	

*Values of m calculated by empirical formulae given in Ref. 42.

**Our data.

All these substances contain NO_2 groups in the molecule. According to current ideas, in the decomposition of a molecule of explosive the NO_2 groups split off and subsequently react with the hydrocarbon fragments of the molecule.

One naturally expects, therefore, that the mass burning rate of volatile explosives will be similar to the mass burning rate of gaseous mixtures based on NO_2 . In fact at atmospheric pressure such a correspondence exists (cf. Tables 2 and 13). High-pressure data for gaseous mixtures exist only for H_2 -NO mixtures (see Table 4).

In addition to the correspondence between the burning rates (at atmospheric pressure) the similarity between volatile explosives containing NO_2 groups and gaseous mixtures based on oxides of nitrogen is shown by the presence of two combustion zones (Fig. 7). In section 1, A it was noted that in the flame of gaseous mixtures based on NO_2 the decomposition $\text{NO}_2 \rightarrow \text{NO} + 0.5\text{O}_2$ and the reaction of oxygen with the fuel occurs in the first zone and the reaction of NO with the fuel in the second zone. A similar phenomenon is observed during the combustion of explosives containing NO_2 groups. The distance Δ between the two zones can be considerable (for example for nitroglycol at 12 atm $\Delta \approx 1.8 \text{ cm}^{37}$).

Δ decreases rapidly with increase of pressure. In photographs the first flame is a narrow strip of low luminosity and the second flame is very bright.

The question of multistage combustion is considered in section 10; here it is noted only that if the distance between the neighbouring zones is large (millimeters or, still more so, centimeters), then in practice only the reaction zone nearest to the unburnt mixture has an effect on the burning rate. Consequently if a connection is being sought between the burning rate and the combustion temperature, the final (equilibrium) combustion temperature should not be used. Consequently it is necessary to introduce the concept of the effective combustion temperature $T_{\text{eff}}^{45,47}$.

T_{eff} is evaluated in Ref. 47 by two different methods:

(1) T_{eff} is calculated according to equation (7) (for $T_c = T_{\text{eff}}$), starting from the experimental value of the temperature coefficient β and the empirical value of the activation energy $E = 37 \text{ kcal/mole}$, which was chosen on the basis of thermal decomposition data and also of data on the bond energy RO-NO_2 .

(2) T_{eff} was measured by means of a thermocouple and was taken to be the temperature where a plateau or a decided change of curvature was observed on the oscillograph.

Approximate values of the equilibrium combustion temperature T_e are given in Refs. 42 and 47. In the present case the approximate nature of the evaluation T_{eff} and of the calculation of T_e is not particularly significant since the main conclusion is that the value of T_{eff} is considerably lower than T_e (Table 14).

TABLE 14.

Value of equilibrium and effective combustion temperature
for a series of volatile explosives

Explosive	p, atm	$T_{\text{eff}}, ^\circ\text{K}^{47}$		$T_e, ^\circ\text{K}^{47}$
		Calculated by equation (15)	Experimental (thermocouple)	
Nitroglycol	1	1390	1400	3400
	5	-	1600	3400
Tetryl	1	1470	1400	2800
	5	-	1500	2800
	10	-	1600	2800
	20	1630	-	2800
Nitroglycerine (gelatinized)	1	1350	-	3300
Methyl nitrate	1	1180	-	3200
Cyclonite (RDX)	1	1700	-	3300

However, substances with a high equilibrium (thermodynamic) combustion temperature can have a higher value of T_{eff} than substances with a low value of T_e . Thus a correspondence can be observed between the burning rate and the equilibrium combustion temperature. Such a correspondence was observed⁴² in the series trotyl (TNT), picric acid, tetryl, cyclonite, but not for PETN (pentaerithritol tetranitrate) and dynamite (Table 15).

TABLE 15

Burning rate and equilibrium combustion temperature
for some volatile explosives

Explosive	$T_e, ^\circ K$	$m, \text{gm cm}^{-2} \text{sec}^{-1}$ (100 atm)	Explosive	$T_e, ^\circ K$	$m, \text{gm cm}^{-2} \text{sec}^{-1}$ (100 atm)
Trotyl (TNT)	1980	0.756	Dynamite	3090	1.02
Picric acid	2475	0.945	Cyclonite (RDX)	3510	3.06
Tetryl	2775	1.55	PETN	3880	1.93

However calculations of the activation energy, using formula (10) and assuming that $T_c = T_e$ for the series of substances, gave excessively high values 100-150 kcal/mole instead of the usual 30-50 kcal/mole.

It is possible that for gaseous mixtures based on oxides of nitrogen there is no correspondence between the burning rate and the equilibrium combustion temperature since the second (high temperature) zone has little effect on the burning rate.

B DEPENDENCE OF BURNING RATE ON PRESSURE

For all the volatile explosives studied, the burning rate increases monotonically with increase of pressure. Moreover for the most volatile explosives the function $u(p)$ shows a dependence close to direct proportionality (Table 16).

For condensed systems as well as for gaseous mixtures an approximation is made to the real curve $m(p)$ or $u(p)$ by using a function of p with exponent ν

$$m = \rho u \sim u = bp^\nu \quad (2)$$

(where $\rho = f(p)$ is the density of the initial condensed system). However in the literature two-term formulae of the following form are often used

$$u = a + bp \quad (2')$$

and

$$u = a + bp^\nu \quad (2'')$$

Obviously formulae (2) and (2') are special cases of formula (2'') (corresponding to $a = 0$ and $\nu = 1$ respectively).

TABLE 16
Dependence of burning rate of volatile explosives on pressure

No.	Substance	$\delta = \frac{\rho}{\rho_{\max}}$	Coefficients in formulae $m(\text{gm cm}^{-2} \text{ sec}^{-1}) = a + b p^{\nu}$			Pressure, atm	Reference
			a	b	ν		
1	Methyl nitrate ($\rho_{\max} = 1.21 \text{ gm/cm}^3$)	1.0	0.01	0.133	1.0	0.175-2.0	[35]
2			-	0.141	0.99	0.5-1.5	[35]*
3	Nitroglycol ($\rho_{\max} = 1.50 \text{ gm/cm}^3$)	1.0	0.0025	0.039	1.0	1-12	[35]
4			-	0.0415	0.97	1-12	[35]*
5	PETN ($\rho_{\max} = 1.77 \text{ gm/cm}^3$)	~1.0 0.98	-	0.0193	1.0	15-750	[42]
6			-	0.028	0.96	15-100	[43]
7			-	0.0173	1.0	500-1500	[44]
8	Dynamite ($\rho_{\max} = 1.67 \text{ gm/cm}^3$)	~1.0	0.118	0.009	1.0	20-100	[42]
9			-	0.034	0.74	20-100	[42]*
10	Cyclonite (RDX) ($\rho_{\max} = 1.80 \text{ gm/cm}^3$)	~1.0	0.9	0.0216	1.0	100-1000	[42]
11			-	0.07?	0.82	10-1000	[42]*
12	Octogen (HMX)	0.875	-	0.0436	0.90	12-205	[200]*
13	Picric acid ($\rho_{\max} = 1.81 \text{ gm/cm}^3$)	~1.0	0.14	0.008	1.0	25-950	[42]
14			-	0.036	0.68	25-80	[42]*
15			-	0.0101	0.97	80-950	[42]*
16	Trotyl (TNT) ($\rho_{\max} = 1.66 \text{ gm/cm}^3$)	~1.0	0.04	0.00716	1.0	20-950	[42]
17			-	0.022	0.75	35-100	[42]*
18			-	0.007	1.0	100-950	[42]*
19			-	0.025	0.77	28-105	[43]
20		0.98	-	0.0065	1.0	500-4000	[44]

*The coefficients in the formula $m = b p^{\nu}$ have been calculated here from the experimental data in the references cited.

In practice the two-term formulae (2') and (2'') can relate experimental results over a much wider range of pressures than the corresponding single-term ($a = 0$) formulae (compare No. 13 with 14, 15 and 16 with 17, 18, Table 16). The single-term formula (2) can be used as successfully by dividing the whole range of pressure into the necessary number of portions, since such a form of dependence $u(p)$ follows from the theory of Zeldovich and Frank-Kamenetsky. Moreover, it is shown in section 15 that only formula (2) is suitable for calculating the pressure in the combustion chamber of a rocket motor with solid fuel. Further, an analysis of the literature data shows that in some cases two-term formulae (2') and (2'') were used without sufficient foundation and these same data could with the same degree of accuracy be approximated using the single-term formula (2) over the same (or even a wider) pressure range. Thus, for example, in Fig. 8, where the experimental points for cyclonite (RDX) and dynamite⁴² are plotted in $\log m$, $\log p$ coordinates, the full lines, constructed according to formula (2), give a much better approximation for the data at low pressures (including at $p = 1$ atm abs) than the dashed lines, constructed from the two-term formula (2'), used in Ref. 42.

The data given in Table 16 show that at high pressures (> 100 - 200 atm) the value of the exponent ν (in the formula $u = bp^\nu$) is very close to unity (except for cyclonite $\nu \approx 0.82$). The value of ν is also close to unity for oxygen gas mixtures and also for a H_2 -NO mixture (see section 1, C). This coincidence is unlikely to be accidental. The presence of the relationship $m \propto p$ is usually regarded as a strong argument in support of the idea that the rate-controlling step in the combustion zone is a bimolecular reaction.

However for picric acid, trotyl (TNT) and tetryl the relationship $u(p)$ is almost a direct proportion in the high pressure range and shows much less dependence on p at 'medium' pressures (for tetryl at 200 - 950 atm $\nu = 1$, but at 10 - 200 atm $\nu \approx 0.7$). In other words if the burning rate falls rapidly at high pressures with decrease in pressure, then at 'medium' pressures it falls more slowly and the experimental points will be further and further above the straight line $m = bp$ corresponding to high pressures. Such an increase, relative to the straight line $m = bp$, in burning rate is possibly connected with the effect studied in Ref. 201. It was shown there that addition of 5% of finely ground wood charcoal increases the burning rate of PETN at 12 - 80 atm, the increase being greatest at the lowest pressure.

The exponent ν is correspondingly reduced (for pure PETN $\nu = 0.95$ and for PETN with 5% wood charcoal $\nu = 0.60$ to 0.65). During the combustion of explosives with high fuel excess (especially trotyl (TNT)) a great deal of soot is formed in the combustion zone, which may result in reduction of ν .

C DEPENDENCE OF BURNING RATE ON INITIAL TEMPERATURE

As the initial temperature T_0 is increased the burning rate of condensed explosives rises monotonically. Thus, as for gaseous mixtures, the relationship $u(T_0)$ or $m(T_0)$ may be characterized by the formula⁶

$$u \propto m \propto e^{-E/2RT_0} \quad (13)$$

where $T_0 = f(T_e)$. For condensed explosives usually $T_0 = T_{\text{eff}} < T_e$ (see section 2,A) and therefore the form of the function $T_0 = f(T_e)$ cannot be established by general considerations.

This difficulty may be avoided by using the dependence of u directly on T_0 although naturally such a dependence does not afford such a clear cut physical meaning as that of equation (13). Thus in Ref.35 the relationship used is in the form

$$\frac{1}{u} = a - bT_0. \quad (14)$$

The function $u(T_0)$ is also expressed in terms of the ratio of the burning rates u_{T_02}/u_{T_01} for given initial temperatures and of the temperature coefficient $\beta_u = d \ln u / dT_0 \approx \beta_m = d \ln m / dT_0$.

Over small intervals the experimental points are often equally satisfactorily grouped about a straight line whether the coordinates $1/u, T_0$ (as required by equation (14)) or the coordinates $\log u, T_0$ (which correspond to a certain constant value $\beta = d \ln u / dT_0$ (Fig.9)) are used.

For most explosives the function $\rho(T)$ has not been determined, but there is no foundation for concluding that there is a stronger temperature dependence than for ordinary solid and liquid substances (the coefficient of volumetric expansion of solid bodies is 10^{-4} degree⁻¹ and of liquids 10^{-3} degree⁻¹). Hence in the temperature interval 0-100-200°C ρ can be taken as constant, and thus the temperature coefficient of linear and mass burning rate will be the same.

When the interval is increased, it has to be divided into several portions and the real relationship, $u(T_0)$, has to be approximated separately for each portion which not infrequently results in the appearance of a variety of types of inflection and discontinuity which scarcely exist experimentally. The values of the temperature coefficient for a series of volatile explosives are given in Table 17.

TABLE 17

Value of temperature coefficient for linear burning rate
 $\beta = d \ln u / dT_0$ for a series of volatile explosives

Substance	p, atm abs	$\beta \cdot 10^3$, deg ⁻¹	Ref.	Temperature, °C
Nitroglycol	1	4.7	31	20-183
		4.8	35	20-95
Nitroglycol, gelatinized (3% collodion)	1	6.5	35	10-95
Nitroglycerine, gelatinized (3% collodion)	1	5.7	35	0-100
Methyl nitrate	1	7.1	35	0-52.8
Diglycoldinitrate	1	6.0	35	19-95
Trotyl (TNT)	1	3.75	47	20-70
Cyclonite (RDX)	1	3.2	47	20-70
Tetryl	1	4.3	47	20-70
	20	3.5	47	20-70

From comparison of Tables 17 and 9 it can be seen that for explosives the temperature coefficient $\beta_u \approx \beta_m$ is about 2-3 times larger than β_m for gas-air mixtures. This is in good agreement with the ideas expounded in section 2,A namely, that for volatile explosives containing NO_2 groups combustion takes place in at least two stages and only the first of these (the low-temperature stage) has any significant effect on the burning rate.

As has already been noted in section 2,A it was proposed in Refs. 45, 47 that the temperature coefficient could be used for evaluating the effective temperature in the zone which determines the burning rate. For this formula (7) was used

$$\beta_u = E/2RT_c^2 = E/2RT_{eff}^2,$$

hence

$$T_{eff} = \sqrt{\frac{E}{2R \beta_u}}. \quad (15)$$

Thus this problem is the inverse of that solved in section 1, E. There, assuming that the temperature in the zone determining the burning rate is equal to the thermodynamic temperature, the function $u(T_c)$ was used to calculate the activation energy. For volatile explosives the function $u(T_c)$, where $T_c = f(T_0)$, cannot be used for calculating the activation energy since it is not clear how T_{eff} , which determines the burning rate, changes as T_0 changes. Thus in Ref. 47 the activation energy was taken as known in the formula analogous to (7) and $T_c = T_{eff} = f(\beta)$ was calculated.

In studying the combustion of condensed systems it is customary to assume that the activation energy for reactions taking place in the combustion zone ($T > 1000-1500^\circ\text{C}$) is the same as for slow thermal decomposition at $T \approx 100-300^\circ\text{C}$.

This assumption is completely unsupported. However from section 1 it can be seen that, for the combustion of gases, attempts to determine the activation energy for reactions in the combustion zone give such a wide range of values of E that the choice of a particular value appears very arbitrary. Therefore for gaseous as well as for condensed systems one has to take the activation energy in equations (9), (10), and (7) as some empirical constant. The most probable value of E for the combustion of gaseous mixtures is 30-40 kcal/mole. For volatile explosives the data for slow thermal decomposition give values for the activation energy in the range 30-60 kcal/mole and usually 35-45 kcal/mole (Table 18).

TABLE 18

Values of activation energy from data on thermal decomposition
for some volatile explosives³⁵

Substance.	E, kcal/mole	Temperature, °C
Methyl nitrate	39.5	212-239
Nitroglycol	39	85-105
Nitroglycerine	40.3	75-105
	42.6	90-125
	45.0	125-150
	50.0	150-190
PETN	47.0	160-225
PETN in solution	39.5	171-238
Trotyl (TNT)	53.5	220-270
Cyclonite (RDX)	47.5	213-299
Cyclonite (RDX) in solution	41.0	-
Tetryl, liquid	60.0	129.9-138.6
	38.4	211-260
Tetryl, solid	52.0	-
	36.6	-

It is also significant that in assessing the value of T_{eff} from (15) an error in the activation energy has a relatively very small effect on the value of T_{eff} , since the activation energy appears under the square root. From section 2,A it can be seen that for nitroglycol and tetryl the value of T_{eff} calculated from (15) with $E = 37$ kcal/mole is in good agreement with the temperature of the first flame measured by a thermocouple (see section 2,A).

If equation (13) is not used for the mass burning rate, but instead the more complete expression (type (10)), then (7) is replaced by

$$\beta = \frac{E}{2KT_c^2} + \frac{n+2}{2T_c} \quad (7')$$

where n is the order of the reaction. Correspondingly for the same value of β the value of T_{eff} will be higher than that from equation (7):

$$T_{\text{eff}}(\gamma') \approx T_{\text{eff}}(\gamma) + \frac{n+2}{4\beta} \quad .$$

However such a refinement of T_{eff} has no real significance, since the concept of effective temperature is approximate. In reality formula (15) can simply be regarded as the definition of effective temperature. In this case the question of increased accuracy is irrelevant.

D DEPENDENCE OF BURNING RATE ON DENSITY

The burning rate (u , mm/sec) of solid explosives can depend on the relative density of the specimen $\delta = \rho/\rho_{\text{max}}$ where ρ is the actual density of a particular specimen, and ρ_{max} the maximum possible density of this specimen. The form of the curve $u(\delta)$ depends on the conditions in which the reaction takes place and on the presence of heat losses. Let us enumerate a few individual cases:

(1) If the reaction takes place in the gas phase and there are no heat losses, the mass burning rate $u\delta = \text{const} \neq f(\delta)$.

(2) In the same conditions but in the presence of heat losses $u\delta$ decreases proportionally as δ decreases.

(3) If the reaction takes place in the condensed phase and the value of δ does not change in the preheating zone upstream of the reaction zone, then in the absence of heat losses $u\delta \propto \sqrt{\lambda \delta^n}$, where λ is the conductivity, cal cm⁻¹ deg⁻¹, and n is the order of the reaction. In particular for $n = 1$ and $\lambda \propto \delta$ we obtain $u\delta \propto \delta$.

(4) In the presence of heat losses (for the conditions given in (3)) the decrease of $u\delta$ proceeds more rapidly as δ decreases.

(5) If the reaction takes place in a melt where $\delta = 1$, then the conditions indicated in (1) and (2) occur.

The above statements (1)-(5) are correct in the absence of the infusion of molten substance or heated gas into the pores of the unburnt substance, i.e. in the absence of convective heat transfer from the combustion zone to the unburnt substance. On the other hand if such an infusion takes place (usually in regions of small δ), the product $u\delta$ can increase with decrease of δ .

Thus the dependence $u(\delta)$ is of great theoretical interest, but its interpretation is rather complex. The dependence $u(\delta)$ has been studied experimentally mainly in connection with the quenching of laminar burning resulting from the infusion of combustion products into the pores of the charge. Much less attention has been given to the question of the dependence $u(\delta)$ for a range of δ where burning is laminar.

TABLE 19

Dependence of mass burning rate of volatile explosives
on the relative density of the charge

Substance	Initial size of particle of explosive	p, atm	$m(\delta)$								Ref.
			δ	0.49	0.54	0.56	0.62	0.64	-	-	
Tetryl		1	$m, \text{gm cm}^{-2} \text{sec}^{-1}$	0.060 0.065	0.065	0.062	0.066	0.064	-	-	35
Cyclonite (RDX)		1	δ	0.38	0.46	0.47	0.56	0.58	0.635	0.645	48
			$m, \text{gm cm}^{-2} \text{sec}^{-1}$	0.040	0.045	0.045	0.047	0.047	0.048	0.048	
PETN	$\sim 5 \mu$	52	δ	0.50	0.51	0.66	0.73	0.88	-	-	200
			$m, \text{gm cm}^{-2} \text{sec}^{-1}$	0.99	0.85	0.86	0.88	0.99	-	-	
	100-400 μ	52	δ	0.60	0.82	0.86	0.90	-	-	-	
			$m, \text{gm cm}^{-2} \text{sec}^{-1}$	0.99	1.00	0.87	0.99	-	-	-	

In Table 19 data are given on the dependence of the mass burning rate on the relative density for three volatile explosives - tetryl, cyclonite (RDX) and PETN. For tetryl and PETN the mass burning rate remains practically constant for changes in δ within the limits of the scatter of results⁴. For cyclonite (RDX) a small increase of m with increase of δ can be observed. At the beginning of this section it was observed that this effect is quite general. This is related to the fact that the heat emission per

⁴For PETN the mass burning rate for laminar burning is also independent of the particle size of the original material from which the charge is pressed. This result seems quite reasonable. Later, however, we shall see that in the combustion of pure NH_4ClO_4 the burning rate can depend to a considerable extent on the particle size of the original material.

unit volume increases in proportion to δ , but the heat losses are almost independent of δ .

Data on the burning rate of octogen (HMX) taken from Ref. 200 are presented in Table 20.

TABLE 20

Values of the mass burning rate of octogen (HMX) for two values of δ at different pressures

Pressure, atm	m, gm cm ⁻² sec ⁻¹		Pressure, atm	m, gm cm ⁻² sec ⁻¹	
	$\delta = 0.54$	$\delta = 0.87$		$\delta = 0.54$	$\delta = 0.87$
12.6	0.48	0.49	154	3.31	3.91
27.2	0.88	-	205	5.13	5.20
52	1.43	1.48			

Thus again m is practically independent of δ .

3 LAMINAR DIFFUSION FLAME DURING THE COMBUSTION OF A GAS OR LIQUID

Diffusion flames of a gas (or of an atomized solid or liquid fuel) are widely used in industrial furnaces. The study of diffusion flames is also of interest in developing methods of dealing with fires in petroleum storage tanks, etc. Although in most industrial cases turbulent diffusion flames are concerned, a considerable scientific research has been made into laminar diffusion flames which are more amenable to theoretical analysis and laboratory investigations. For condensed mixtures, where the particle sizes of the components are small, only laminar diffusion flames are relevant.

A DIFFUSION BURNING OF A JET OF FUEL GAS

During the flow of a jet of fuel gas into a parallel stream of air (or into ambient air) combustion begins at the edges of the jet. Oxygen diffuses into the flame through a layer of combustion products. When the flame approaches the axis of the jet of gas, burning ceases. A simple expression for the height h of the diffusion flame can be obtained from equilibrium considerations

It is essential to note that the diffusion flame cannot approach the rim of the burner because of the occurrence of heat transfer to the burner. Moreover the interdiffusion of the oxidizer and fuel starts inside the burner. Hence near to the top of the burner combustion is taking place in a homogeneous mixture, and diffusive burning starts further downstream. Although the region of homogeneous combustion is small, it is most significant in stabilizing the diffusion flame¹².

$$h(\text{cm}) \propto \frac{v(\text{cm/sec}) \cdot R^2(\text{cm}^2)}{D(\text{cm}^2/\text{sec})} \quad (16)$$

where v is the velocity of the gas, R is the radius of the jet of fuel gas, and D is the diffusion coefficient for the oxidizer diffusing through the combustion products. It is not difficult to obtain a more complete formula for the height of the flame using some simple approximations

$$h = \frac{k \rho_g}{4C_\infty} \cdot \frac{v R^2}{D} \quad (17)$$

where k is the number of grams of oxidizer required to oxidize 1 gram of fuel, ρ_g is the density of the fuel gas, gm/cm^3 and C_∞ is the concentration of oxidizer at a great distance from the flame, gm/cm^3 . In accordance with (17) the height of the flame decreases with increase of C_∞ , resulting for example from a change from air to oxygen*. Obviously equations analogous to (16) and (17) can be used to find the height of the flame for the case where a jet of oxidizer flows into the fuel gas. Experimental data show that the thickness of the reaction zone in diffusion flames is considerably greater than in homogeneous mixtures and at 1 atm abs it can have a value up to 1 cm for condensed mixtures and several millimeters for air mixtures¹². Correspondingly the rate of emission of heat per unit volume of the reaction zone decreases. Thus, for the diffusion flame $\text{CH}_4\text{-O}_2$, the consumption of oxygen amounts to $\sim 6 \cdot 10^{-5} \text{ mole cm}^{-3} \text{ sec}^{-1}$ and $\phi_{\text{max}} \sim 10^1 \text{ cal cm}^{-3} \text{ sec}^{-1}$ whereas in the homogeneous mixture $\text{CH}_4\text{-O}_2$ the corresponding values are $4 \text{ mole cm}^{-3} \text{ sec}^{-1}$ and $\sim 4 \cdot 10^5 \text{ cal cm}^{-3} \text{ sec}^{-1}$.

We will now examine how well the approximate formulae (16) and (17) fit the experimental observations. It follows from these formulae that, other conditions being the same, the height of a flame is proportional to the volumetric consumption $v R^2 \text{ cm}^3/\text{sec}$ (or mass consumption $\rho_g v R^2 \text{ gm cm}^{-2} \text{ sec}^{-1}$) of fuel gas. Consequently $h/v R^2$ should be independent of $v R^2$. The data of Burke and Schumann²³ for a diffusion flame of methane in air are presented in Table 21.

*In diffusion flame research the burning rate is generally not calculated, although it can be determined as the discharge of gas through a ring element of the conical surface of the flame divided by the area of this element. However, the burning rate determined in this way would not be a constant for the mixture, but would depend on the diffusion coefficient for the oxidizer diffusing through the combustion products and on the diameter of the burner.

TABLE 21

Dependence of height of diffusion flame of methane in air on the volumetric consumption ($\pi R^2 v$) of methane²³

Consumption of methane, l/hr	h, cm	$h/\pi R^2 v$	Consumption of methane, l/hr	h, cm	$h/\pi R^2 v$
64.6	25.1	0.389	28.3	11.3	0.40
58.4	22.9	0.392	21.2	8.6	0.405
46.4	18.4	0.396	10.7	3.1	0.29
37.1	14.8	0.40			

It follows from Table 21 that, for a threefold decrease in volumetric consumption, the quantity h/vR^2 remains practically constant and will decrease to any significant extent only for a sufficiently small value of vR^2 .

The data of Wohl, Gazley and Kapp⁵⁰ for a diffusion flame of town gas in air show that the length of flame h for constant volumetric flow which varied from 1 to 100 cm³/sec does not depend on the diameter of the burner over the range 4-10 mm. This is in agreement with formulae (16) and (17).

From formulae (16) and (17) it follows that $h \propto 1/D$. For flames of H₂ in air and CO in air $h_{CO}/h_{H_2} \approx 2.5$ whereas $1/D_{CO \rightarrow CO_2} / 1/D_{H_2 \rightarrow CO_2} = 0.55/0.137 = 4$ (the diffusion coefficients are taken from the data of Hirschfelder; $T = 273^\circ K$).

Formulae (16) and (17) also show that h does not depend on the pressure for constant volumetric flow, calculated under standard conditions (i.e. 1 atm abs and 273°K). This can be seen particularly clearly from (17), where for $\rho_g vR^2 = \text{const} \neq f(p)$; $C_\infty \sim p$; $D \sim 1/p$ and correspondingly $h \neq f(p)$. This result was confirmed experimentally by Burke and Schumann for CH₄ flames, but only for a very narrow pressure range (1-1.5 atm).

B BURNING OF A LIQUID FUEL WITH A FREE SURFACE

Let us consider the diffusion burning of a liquid poured into a cylindrical vessel. If the level of the liquid relative to the end of the tube and the temperature of the walls of the tube are kept constant, combustion is stationary. For small tube diameters ($d \leq 10$ mm for combustion in air at 1 atm abs⁴⁹) burning is laminar. This combustion regime is considered here.

The height h and shape of the flame during diffusion burning of a liquid and a gas conform to the same laws. In particular, if the rate of burning of a liquid is w , then the condition $h/w (d/2)^2 = \text{const}$ should be fulfilled. In fact, for petrol, kerosene, diesel fuel, gas oil and ethyl alcohol, the value of $h/w (d/2)^2$ does not change much and shows no trend as d changes^{49,51}. The following values have been obtained for gas oil:

d , mm	3.7	5.0	6.0	7.1	11	20
w , mm/sec	0.155	0.085	0.068	0.055	0.040	0.018
h , cm	3.0	4.0	4.4	4.9	7.9	11.8
$h/w (d/2)^2 \cdot 10^{-3} \text{ sec/cm}^2$	5.7	7.5	7.2	7.1	6.5	6.4

However, for diffusive combustion of a gas the velocity of the jet of gas is controlled by the experimenter. On the other hand for a liquid the rate of burning establishes itself and depends on the thermodynamic parameters of the liquid and on the conditions of diffusion.

The velocity w differs considerably from the normal rate of burning in homogeneous systems. On the one hand it refers only to the pure fuel. Moreover, for each gram of fuel consumed an additional 1.5-3.5 gm of oxygen (depending on the nature of the fuel) is required. Therefore the mass rate of burning of pure fuel $\rho_l w$ (where ρ_l is the density of the liquid fuel) is approximately 2.5 to 5 times lower than the mass burning rate of the corresponding stoichiometric mixture of fuel and oxygen.

However, on the other hand, $\rho_l w$ is related not to the surface of the combustion front, but to the cross-sectional area of the tube. Data⁵¹ on the height of the flame show that this raises the rate of burning about 10-30 times, but the overall rise is shown to be 2-10 times. However such a comparison with the rate of burning of homogeneous systems is only of formal interest since, as shown later, the rate of burning of a liquid depends only slightly on the total height of the flame.

The parameters having an effect on the burning rate of a liquid (w) are now examined.

(1) As the burner diameter is increased the rate of laminar combustion of a liquid decreases rapidly (Fig.10). When d is further increased (when combustion already ceases to be laminar) the burning rate ceases to decrease and then increases somewhat, evidently approaching some limit; however, this part of the curve $w(d)$ is not examined here.

The maximum experimental value of the burning rate⁵¹ (measured in the narrowest tubes) amounts to $\approx 0.022 \text{ gm cm}^{-2} \text{ sec}^{-1}$ for petrol and $\approx 0.016 \text{ gm cm}^{-2} \text{ sec}^{-1}$ for kerosene (at 1 atm abs).

(2) The burning rate of a liquid increases with an increase in oxygen concentration in the surrounding medium (Fig. 11): on changing over from air (21% O_2 by volume) to a mixture of 50% O_2 + 50% N_2 , the burning rate of petrol increases approximately 2.1 times and that of diesel fuel 3.3 times.

(3) The burning rate of liquids increases rapidly with increase of pressure⁵². Thus for n-octane in a quartz crucible of diameter⁶ 11.3 mm in a manometric bomb the following values were obtained (ρ_l is the density of the liquid):

p_{O_2} , atm	15	20	30	40	50	60
$\rho_l w$, $\text{gm cm}^{-2} \text{ sec}^{-1}$	0.0052	0.0074	0.0120	0.0170	0.0230	0.0280

Comparison of these results with those in Tables 4 and 13 shows that the value of $\rho_l w$ for n-octane at high pressures is one or two orders of magnitude lower than the burning rate of homogeneous air mixtures (to say nothing of oxygen mixtures) and $1\frac{1}{2}$ to 2 orders of magnitude lower than the burning rate of volatile explosives. The dependence of the mass burning rate of n-decane, benzene, gas oil and diesel fuel on the pressure can be expressed by the empirical formula $\rho_l w \propto p_{\text{O}_2}^n$ where p_{O_2} is the pressure of oxygen and the exponent $n = 0.96$ to 1.07 ($p_{\text{O}_2} = 10$ to 40 atm). For n-octane the exponent n decreases as the diameter of the crucible increases (from $n = 1.2$ at $d_{\text{equ}} = 11.3$ mm to $n = 0.83$ at $d_{\text{equ}} = 22.6$ mm for the range $p_{\text{O}_2} = 15$ to 60 atm). The presence of the strong dependence of $\rho_l w$ on p is related to the convective transfer of oxygen to the flame⁵². However with increase of d_{equ} the exponent n did not increase but decreased. It is not clear whether combustion was laminar at high pressures.

(4) As the distance Δ between the surface of the liquid and the rim of the burner increases (during the experiment $\Delta = \text{const} + f(t)$) the burning rate decreases:

⁶Equivalent diameter calculated from the free area of liquid $d_{\text{equ}} = \sqrt{4S/\pi}$.

Δ , mm	w, mm/sec		Δ , mm	w, mm/sec	
	Ethyl alcohol	Kerosene		Ethyl alcohol	Kerosene
0	0.060	0.055	4.5	0.028	0.022
0.5	0.052	0.047	6.5	0.017	0.0067
2.6	0.042	0.040			

At a sufficiently high value of Δ burning ceases.

(5) The burning rate depends on the nature of the liquid. For example the following results have been obtained⁵¹:

Fuel liquid	w, mm/sec		Fuel liquid	w, mm/sec	
	d = 6 mm	d = 20 mm		d = 6 mm	d = 20 mm
Car petrol	0.300	0.057	Diesel fuel	0.070	0.028
Tractor kerosene	0.1065	0.032	Gas oil	0.068	0.018

The value of the ratio of w for the fastest burning to w for the slowest burning liquid (w_{\max}/w_{\min}) for the same value of d is 3 to 4.5, i.e. about the same as the analogous relationship for air mixtures or volatile explosives at 1 atm abs. Values of w for 30 different liquids in quartz burners of large diameter (62 and 106 mm) have been obtained⁴⁹. In particular the following values of w (in mm/sec) were obtained for $d = 62$ mm:

Benzene	0.052	Car petrol	0.028
Ethyl alcohol	0.048	Carbon bisulphide	0.028
Toluene	0.045	Acetone	0.023
Turpentine	0.040	Methyl alcohol	0.020
Aviation petrol	0.035	Kerosene	0.017
Xylene	0.033	Gas oil	0.013

In this case $w_{\max}/w_{\min} = 4$. The effect of the nature of the liquid on the value of w decreases somewhat with the increase in diameter of the burner.

(6) The burning rate of a liquid decreases with increase in the conductivity of the material of the burner and the thickness of its walls⁴⁹. Thus, for example, the following results were obtained for ethyl alcohol:

Burner	w, mm/sec	
	d = 8 mm	d = 10 mm
Glass	0.077	0.057
Steel	0.072	-
Copper	-	0.045

The factors which determine the rate of burning of a liquid with a free surface may now be examined. It can be assumed that it is basically those parts of the flame nearest to the surface of the liquid which influence the value of w . Hence the relation between the burning rate w and the height of the flame h is unidirectional: the height of the flame is proportional to w (see above), but the burning rate depends only slightly on the full height of the flame.

The amount of substance reacting in that part of the flame which has a significant effect on the burning rate (in the 'zone of influence') is limited by the rate of supply of oxidizer from the surrounding volume, since it increases with increase in concentration of oxidizer in the volume. The quantity of heat which is emitted within the boundary of the zone of influence naturally depends on the nature of the liquid, although the value of the heat of combustion, calculated for a mole of oxygen (Q_c kcal/mole O_2), for the majority of liquid fuels lies within very narrow limits:

Methyl alcohol	108	Ethyl ether	100
Glycerine	101.5	Xylene	99.5
Benzene	101	Acetone	98.2

This result seems reasonable, as the heats of combustion even for hydrogen and carbon (for one mole of O_2) do not differ very much (115.6 and 94 kcal/mole O_2) and the contribution of the heat of formation of a liquid is not very significant.

However the flow of heat q from the flame to the surface of the liquid can depend to a considerable extent on the nature of the liquid; in particular the flow by radiation is large for the smoky flames of benzene, xylene, etc, and small for the transparent flames of the lower alcohols and ethers.

This heat flow is used up in heating and evaporating the liquid

$$q = \rho_l w \frac{\pi d^2}{4} [c_l(T_{ev} - T_o) + Q_{ev}] \quad (18)$$

Hence

$$w = \frac{q}{\frac{\pi d^2}{4} \rho_l [c_l(T_{ev} - T_o) + Q_{ev}]} \quad (18')$$

where c_l is the specific heat, $\text{cal gm}^{-1} \text{deg}^{-1}$, and Q_{ev} is the heat of evaporation of the liquid, cal gm^{-1} . Hence the effect of the nature of the liquid on the value of w is connected not only with changes in the value of q but also with changes in the thermodynamic properties of the liquid.

The data in Table 22 show (in agreement with the conclusions of Ref. 49) that there is a correspondence between the burning rate and the heat losses $\rho_l [c_l(T_{ev} - T_o) + Q_{ev}]$ in heating and evaporating the liquid (see the series benzene, xylene, glycerine and ethyl ether, acetone, methyl alcohol).

The influence of q on the burning rate is shown by comparison of benzene with ethyl ether (see Table 22) when the value of $\rho_l [c_l(T_{ev} - T_o) + Q_{ev}]$ decreases approximately 1.6 times but the burning rate, nevertheless, decreases (apparently owing to the decrease in the radial flow).

TABLE 22

Burning rate and heat expended in preheating and evaporating
unit volumes of liquid fuels

Liquid fuel	$w, \text{mm sec}^{-1}$	$\rho_l [c_l(T_{ev} - T_o) + Q_{ev}] \text{ cal cm}^{-3}$
Benzene	0.052	105
Ethyl ether	0.048	67.5
Xylene	0.033	116.5
Acetone	0.023	120
Methyl alcohol	0.020	230
Glycerine	0.0067	361

A few remarks on the relationships $w(p)$, $w(d)$, etc, can be made.

(a) The increase in w with increase in p is related not only with the increased convective heat transfer but also with the fact that the flame burning as a homogeneous mixture⁶ (at the tip of the burner) approaches the surface of the liquid as p increases.

(b) The decrease in w with increase in d is because the flow of heat from the flame as a result of thermal conductivity takes place only at the burner periphery and is proportional to the burner diameter¹⁹. The heat transfer by radiation is proportional to the area of cross-section of the burner. Hence $w \propto (ad + bd^2)/d^2 = a/d + b$, i.e. w decreases with increase of d .

(c) Some portion of the heat released in the flame is removed along the walls of the burner. Part of this heat is used in heating the surface layers of the liquid (and increases w). However owing to the low burning rate of the liquid the greater part of the heat carried along the wall is lost since the burner is not thermally insulated and this lowers w .

4. COMBUSTION OF SOLID PARTICLES AND DROPS OF LIQUID

The combustion of atomized solid or liquid fuel plays an important role in ram-jets, liquid propellant rocket engines, diesel engines and industrial furnaces using coal dust or liquid fuel. It should be noted that in the combustion of a gas there is the possibility that carbon particles are formed in the flame (both in diffusion and homogeneous flames, especially at high pressures¹²). Consequently combustion is protracted and the height of the flame increases.

The most important parameters for the combustion of an atomized fuel are the ignition delay τ_{ig} and the duration of combustion τ_c , since they determine the necessary dimensions of the combustion chamber.

The burning rate of a fuel particle generally depends both on the rate of supply of oxidizer from the surrounding volume and the rate of the reaction at the combustion front. This can be expressed quite clearly²⁶. Let the concentration (in gm cm^{-3}) of the oxidizer be C_∞ in the surrounding volume

⁶A homogeneous mixture is formed because the flame is situated at some distance from the edge of the burner (this distance is limited by the rate of heat loss to the burner walls), but the mixing of the fuel vapour with the gaseous oxidizer starts directly at the burner outlet.

and C_ϕ at the combustion front. For a stationary (steady) process the amount of oxidizer reacting in unit area of combustion front in unit time is that which is supplied by diffusion from the surrounding volume. For a first order reaction this can be expressed by

$$k_{\text{kin}} C_\phi = k_{\text{dif}} (C_\infty - C_\phi) \quad (19)$$

where k_{kin} and k_{dif} are the reaction rate constant and the diffusion coefficient, cm sec^{-1} . Hence we find the concentration of oxidizer in the combustion front is $C_\phi = C_\infty k_{\text{dif}} / (k_{\text{kin}} + k_{\text{dif}})$. Correspondingly the rate of consumption of oxidizer in the combustion front m_{ox} (in $\text{gm cm}^{-2} \text{sec}^{-1}$) is given by

$$m_{\text{ox}} = k_{\text{kin}} C_\phi = \frac{C_\infty}{1/k_{\text{dif}} + 1/k_{\text{kin}}} \quad (20)$$

From this it is easy to calculate the rate of burning of a particle³⁴. If $k_{\text{dif}} \gg k_{\text{kin}}$, i.e. diffusion does not limit the rate of the process, the combustion is kinetically controlled and $C_\phi \approx C_\infty$; $m_{\text{ox}} \approx k_{\text{kin}} C_\infty$. On the other hand if $k_{\text{dif}} \ll k_{\text{kin}}$, i.e. the reaction rate is very high, the combustion is diffusion controlled and $C_\phi \approx 0$; $m_{\text{ox}} \approx k_{\text{dif}} C_\infty$.

Experimental data show that the combustion of drops of liquid fuel and metal particles usually follow the laws characteristic of the diffusion controlled regime tolerably well (see below).

A FORMULA FOR THE RATE OF DIFFUSION BURNING OF A SPHERICAL PARTICLE

The combustion of a single particle of fuel in a gas at rest will be examined. The diffusion of the i th gas to the particle can be expressed by the equation

$$D \frac{d}{dr} \left(r^2 \frac{dC_i}{dr} \right) - v r^2 \frac{dC_i}{dr} = 0 \quad (21)$$

where C_i is the molar concentration, mole cm^{-3} ; D is the diffusion coefficient $\text{cm}^2 \text{sec}^{-1}$; v is the velocity of the gas for Stefan flow, cm sec^{-1} . It is assumed that the density of the gas and the diffusion coefficient are

independent of the coordinates. The quasistationary solution will be considered.

The continuity equation, since $\rho_g \neq f(r)$, is

$$v r^2 = \text{const} = v_\phi r_\phi^2 \quad (22)$$

where r_ϕ is the radius of the combustion front, and $v_\phi = v|_{r=r_\phi}$.

The boundary conditions are

$$C_i|_{r \rightarrow \infty} = C_{i\infty}; \quad C_i|_{r=r_\phi} = C_{i\phi} \quad (23)$$

Integrating (21) and taking into account (22) and (23) we obtain

$$\left(\frac{dC_i}{dr} \right)_{r_\phi} = \frac{v_\phi}{D} \cdot \frac{C_{i\infty} - C_{i\phi}}{\frac{v_\phi r_\phi}{c_\phi D} - 1} \quad (24)$$

The flow of the i th gas to the combustion front is equal to

$$q_{i\phi} = -D \left(\frac{dC_i}{dr} \right)_{r_\phi} + v_\phi C_{i\phi} = v_\phi \left(C_{i\phi} - \frac{C_{i\infty} - C_{i\phi}}{\frac{v_\phi r_\phi}{c_\phi D} - 1} \right) \quad (25)$$

The value of $C_{i\infty}$ is known, since the initial composition of the gas is given. However the values of $C_{i\phi}$ and v_ϕ cannot be predicted but must be deduced from supplementary conditions. The most important of these that must be fulfilled is that there is no accumulation of a substance in the combustion front. In other words the flow of each element (e.g. O) of the gases transferred to the combustion front (e.g. O_2) must be equal to the flow of this element in the composition of the gases transferred from the combustion front (e.g. H_2O , CO_2). As an illustration of the method, consider the combustion of a hydrocarbon fuel in air assuming that the products of

combustion are only CO_2 and H_2O . Then the above mentioned condition can be written in the form*

$$(q_{\text{O}_2})_\phi + 0.5 (q_{\text{H}_2\text{O}})_\phi + (q_{\text{CO}_2})_\phi = 0 . \quad (26)$$

Here the flows q_i are expressed in mole $\text{cm}^{-2} \text{sec}^{-1}$; correspondingly equation (26) denotes that the number of moles of oxygen transferred to the combustion front (in unit time through unit area) is equal to the number of moles of oxygen in the composition of the products of combustion transferred from the combustion front. Furthermore it is obvious that

$$(q_{\text{N}_2})_\phi = 0 . \quad (27)$$

If in a molecule of the fuel the ratio of the number of atoms of hydrogen to those of carbon is equal to $n_{\text{H}}/n_{\text{C}}$ then in the above example

$$\frac{2(q_{\text{H}_2\text{O}})_\phi}{(q_{\text{CO}_2})_\phi} = \frac{n_{\text{H}}}{n_{\text{C}}} . \quad (28)$$

Further, for diffusion-controlled combustion the concentration of oxidizer, and the concentration of the fuel, in the combustion front is exceedingly small. In the present example

$$(C_{\text{O}_2})_\phi \approx 0 . \quad (29)$$

*This is only an approximation, since in addition to the flow of CO_2 and H_2O from the combustion front there exists a small flow of combustion products (and nitrogen) to the surface of the drop opposed to the flow of products of the fuel. For an exact representation of the problem, in addition to the solution of the diffusion equation (21) for the external (relative to the combustion front) region, the analogous equation for the internal region (between the combustion front and the drop) should be solved and take into account the presence of a sharp discontinuity of density and of gas velocity at the front. However, because of the numerous simplifications made at the start of the solution ($\rho_g \neq f(r)$; $D \neq f(r)$), the schematic composition of the products of combustion, and the fact that the solution is for a quasistationary state, a more exact representation is not considered justified.

Finally from the equation of state of a real gas

$$\sum_i C_{i\phi} = p/RT \quad (30)$$

It is convenient to change from the dimensional concentration $C_i = (m_i/\mu_i)/V$ mole cm^{-3} to the dimensionless volumetric concentration $\vartheta_i = V_i/v$. Substituting for C_i in the equation of state $p V_i = (m_i/\mu_i) RT = C_i V RT$ we obtain $C_i = \vartheta_i P/RT$ and condition (30) can be written in the form:

$$\sum_i \vartheta_{i\phi} = 1 \quad (30')$$

In equations (26)-(29) C_i can simply be replaced by ϑ_i since the multiplication factor P/RT cancels out.

The systems (26)-(29), (30') consists of five equations and five unknowns: $(\vartheta_{\text{H}_2\text{O}})_\phi$, $(\vartheta_{\text{CO}_2})_\phi$, $(\vartheta_{\text{N}_2})_\phi$, $(\vartheta_{\text{O}_2})_\phi$ and v_ϕ which can be determined from this system. Moreover the expression for v_ϕ can be obtained in the form:

$$v_\phi = \frac{D}{r_\phi} \ln(1 + A) \quad (31)$$

where

$$\begin{aligned} A &= \frac{[(\vartheta_{\text{O}_2})_\infty + 0.5 (\vartheta_{\text{H}_2\text{O}})_\infty + (\vartheta_{\text{CO}_2})_\infty] - [0.5 (\vartheta_{\text{H}_2\text{O}})_\phi + (\vartheta_{\text{CO}_2})_\phi]}{0.5 (\vartheta_{\text{H}_2\text{O}})_\phi + (\vartheta_{\text{CO}_2})_\phi} \\ &= \frac{(\vartheta_{\text{N}_2})_\infty - (\vartheta_{\text{N}_2})_\phi}{(\vartheta_{\text{N}_2})_\phi} \quad (32) \end{aligned}$$

For the combustion of a single drop in air the approximation can be made that $(\vartheta_{\text{H}_2\text{O}})_\infty \approx 0$, $(\vartheta_{\text{CO}_2})_\infty \approx 0$, $(\vartheta_{\text{O}_2})_\infty = 0.21$, $(\vartheta_{\text{N}_2})_\infty \approx 0.79$.

Consider the equation relating the burning rate of a particle with the rate of diffusion of the oxidizer to the combustion front. Let 1 mole of fuel react with k moles of oxidizer. Then

$$4\pi r_\phi^2 (q_{O_2})_\phi \mu_f dt = -k 4\pi r_d^2 dr_d \rho_f \quad (33)$$

where μ_f is the molecular weight of the fuel, t is time, r_d is the radius of the drop (particle) of fuel, and ρ_f is the density of the fuel (solid or liquid) gm cm^{-3} .

Hence the rate of burning of the particle is

$$w = \frac{dr_d}{dt} = - \left(\frac{r_\phi}{r_d} \right)^2 \frac{(q_{O_2})_\phi \mu_f}{k \rho_f} \quad (34)$$

Substituting for $(q_{O_2})_\phi$ in (34) yields

$$w = \frac{1}{r_d} \cdot \frac{r_\phi}{r_d} D \frac{p}{RT} \frac{(q_{O_2})_\infty \mu_f}{k \rho_f} \frac{\ln(1+A)}{A} \quad (35)$$

where $D = D_0 (p_0/p)(T/T_0)^n$ where $p_0 = 1 \text{ atm}$, $T_0 = 273^\circ\text{K}$, $D_0 = D|_{p_0, T_0}$ and $n = 1.75$ to 2.0 .

The ratio r_ϕ/r_d can be obtained from the condition that in the stationary regime* the quantity of heat supplied to the particle is equal to the loss of heat in the evaporation of the particle

$$\lambda' \left. \frac{dT}{dr} \right|_{r_d} = \rho_f w Q_{ev} = \rho' v_d' Q_{ev} \quad (36)$$

*During the combustion of a particle a steady regime of two types is possible: (1) if the thermal conductivity of the particle and the interval of time after the start of combustion are sufficiently large, the temperature becomes the same at any point of the particle and is independent of time; (2) if the thermal conductivity of the particle is very small (or if the combustion of a liquid in a burner with tracer powder is being studied) a stationary heating wave is established at the particle surface.

where λ' , ρ' , v_d are the thermal conductivity, density and velocity (at the surface of the drop) of the fuel vapour. The temperature gradient $\left. \frac{dT}{dr} \right|_{r_d}$ is

given by the heat conduction equation $\frac{a'}{2} \frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) - v' \frac{dT}{dr} = 0$ in the range $r_d \leq r \leq r_\phi$ for the boundary conditions $T|_{r_d} = T_d = f(p)$ and $T|_{r_\phi} = T_\phi$.

Whence

$$\left. \frac{dT}{dr} \right|_{r_d} = \frac{v'_d}{a'} \frac{T_f - T_d}{e^{\frac{v'_d r_d}{a'}} \left(1 - \frac{r_d}{r_f} \right) - 1} \quad (37)$$

where $a' = \lambda'/\rho c'$ is the temperature transfer coefficient of the fuel vapour. Substituting (37) in (36) gives

$$w = \frac{\lambda'}{c' \rho_f} \frac{1}{r_d \left(1 - \frac{r_d}{r_\phi} \right)} \cdot \ln \left[1 + \frac{c' (T_\phi - T_d)}{Q_{ev}} \right] \quad (38)$$

The two equations (37) and (38) have two unknowns w and r_ϕ/r_f . Hence

$$w = - \frac{dr_d}{dt} = \frac{1}{r_d \rho_f} (N + L) \quad (39)$$

$$\frac{r_\phi}{r_d} = 1 + \frac{L}{N} \quad (40)$$

where

$$L = \frac{\lambda'}{c'} \ln \left[1 + \frac{c' (T_\phi - T_d)}{Q_{ev}} \right]$$

and

$$N = D_0 T^{n-1} \frac{p_0}{RT_0^n} \frac{1}{k} (\vartheta_{O_2})_\infty f \frac{\ln(1+A)}{A} \quad .$$

It should be noted that N does not depend on pressure and L depends only slightly on pressure (with increase of pressure T_d can increase and Q_{ev} decrease). Integrating (39) gives

$$d^2 = d_0^2 - nt \quad (41)$$

$$\tau = d_0^2/n$$

where d_0 is the diameter of the particle at $t = 0$, $n = 8(N + L)/\rho_f$, and τ is the time of burning of the particle (from $d = d_0$ to $d = 0$). Hence the time of burning of the particle is proportional to the square of its initial diameter and does not depend on the pressure.

B EXPERIMENTAL DATA ON THE COMBUSTION OF PARTICLES

In studying the combustion of particles and drops at least three different methods are used.

(1) The drop or particle moves freely in a stream of gas and its combustion time is measured.

(2) The drop or particle is suspended on a fine filament, usually quartz, and its radius is measured as a function of the time and the total time of burning is also measured.

(3) A liquid fuel permeates from inside a small porous sphere and burns on the surface of the latter. Measurements are made of the rate of consumption of fuel, i.e. its rate of burning.

In the first and second methods the combustion is non-stationary and quasistationary whereas in the third method it is stationary. The first method is used for drops of size from ~100 microns to a few millimeters and for finer particles from 1-10 microns for solid fuels. The second and third methods are used for relatively large particles ($d > 1$ mm).

First consider the combustion of drops of liquid fuels. A spherically symmetrical flame is observed only in the case of very small drops. For $d > 1$ mm the flame is considerably drawn out (Fig.12) owing to natural convection. Experiments have been made in a free-falling chamber^{55,56} when the flame became spherically symmetrical, but the rate of burning decreased approximately 2 times owing to the absence of convection.

In spite of the distortion of the flame shape many, but naturally not all, experimental results agree with the results deduced from the theory obtained for the spherically symmetrical case. Most important of all is the agreement with theory of the dependence of the burning rate and time of burning on the diameter of the drop. Thus it has been shown^{55,57} that for coordinates d^2 , t the experimental points for seventeen liquids fall on a straight line, i.e. they satisfy equation (41).

It has been shown^{54,58} that the experimental points are in good agreement with the relationship

$$\dot{M} = 4\pi r_d^2 \frac{dr_d}{dt} \cdot \rho_f \propto r_d$$

which is derived from equation (39)*.

The dependence of the time of burning τ on the diameter of a drop d_0^2 has also been studied⁵⁸. Equation (42) predicts that this dependence should be $\tau \propto d_0^2$. This result was obtained for drops of tetralin and paraffin ($d_0 = 150$ to 600 microns). For drops of kerosene the exponent was somewhat higher (~ 2.3).

It has been shown⁵⁴ that the burning rate of ethyl alcohol on a porous sphere of diameter 5.5 mm increases with increase in the concentration of oxygen (in mixtures with nitrogen or helium):

O ₂ , volume %	25	40	63	100
Rate of burning, O ₂ + N ₂	0.0042	0.0057	0.0072	0.0085
gm/sec O ₂ + H _e	0.0055	0.0074	0.0083	0.0085

However the increase in burning rate is less than would be expected from the theory.

The burning rate of drops of furfuryl alcohol, tetralin, decane and amyl acetate increases with increase in pressure⁵⁸ (in general $\propto p^{0.25}$). This result is also not in agreement with the theory expounded above and this may possibly be connected with the effect of convection.

* \dot{M} is the rate of burning of a drop, gm sec⁻¹.

For 1 atm abs the experimental value of n in (41) and (42) for the combustion of organic liquids in air lies between the limits (0.7 to 1.0) $10^{-2} \text{ cm}^2 \text{ sec}^{-1}$. It can be shown that at 1 atm abs the mass burning rate of drops (calculated for unit surface of combustion front taking into account the mass of oxidizer) becomes comparable with the mass rate of burning of homogeneous fuel gas - air mixtures (see Table 1) only for very small drops ($r_d < 10$ microns). By reducing the size of the drop one can obtain very high theoretical burning rates, but such small drops have sufficient time to evaporate completely before ignition.

The combustion of metal particles is most frequently studied under conditions where the particle is free to move in a current of air (or oxygen) and also in the combustion products of a gaseous (or condensed) system (see Figs. 13, 14, 15). In the latter case combustion of the metal takes place at the expense of the reduction of H_2O (to hydrogen) or CO_2 (to CO), etc. In comparison with the experimental results on liquid fuels, there are few results in the literature on the combustion of metal particles; they are also less complete and there is considerable divergence between the works of various authors. Hence a comparison of the experimental results with those deduced from the diffusion theory can only be made within very narrow limits. We have seen that for the combustion of drops of liquid fuels the dependence of the burning rate and of the time of burning on the diameter of a drop is in good agreement with theory (in particular, time of burning $\tau \propto d_0^2$). For particles of metals the dependence $\tau(d)$ was studied within very narrow limits of d and on the basis of a very small number of points. For aluminium $\tau \propto d_0^{1.5}$ was obtained in Ref. 59 and $\tau \propto d_0^{1.8}$ in Ref. 60 (for two points $d_0 \approx 60$ microns and $d_0 \approx 95$ microns). For magnesium $\tau \propto d_0^{2.56}$ and for titanium $\tau \propto d_0^{1.59}$ are given in Ref. 61.

It has been observed⁶⁰ that the time of combustion decreases rapidly with increase in concentration of oxygen. The following values were obtained for aluminium particles ($d_0 = 53$ to 66 microns) in an atmosphere of the products of combustion of the mixture $\text{CO}-\text{O}_2-\text{N}_2$ ($\sim 2500^\circ\text{K}$, 1 atm abs).

O_2 volume %	23.3	30	40	50	60
$\tau \cdot 10^3$, sec	12.7	8.4	6.5	5.4	4.5.

The strong influence of the oxidizer concentration is in agreement with theory. On the other hand the decrease of combustion time of aluminium particles with increase of pressure⁶⁰ (Table 23) does not agree with the diffusion theory and further considerations are required to explain this. It is possible that with increase in pressure combustion becomes more complete and there is an increase in the intensity of combustion and of the combustion temperature of the mixture NH_4ClO_4 - formaldehyde, in the combustion products of which the experiments were carried out. Also, on increase of pressure the concentration of the particles of aluminium in unit volume increases and the radiative heat losses are correspondingly reduced.

TABLE 23

Dependence of combustion time of aluminium particles on pressure

Experiments were conducted in the products of combustion of the mixture NH_4ClO_4 - paraformaldehyde⁶⁰

Content of mixture, % by wt			d_{Al} , microns	$\tau \cdot 10^3$, sec					
NH_4ClO_4	PFA	Al		21 atm	42 atm	63 atm	105 atm	147 atm	189 atm
85	15	0.01	89-103	-	11.5	9.7	7.9	7.3	7.3
90	10	0.1	53-66	9.6	7.4	5.9	4.8	4.7	4.7
95	15	0.01	53-66	5.5	4.2	3.6	3.5	3.5	3.5
76	24	0.01	53-66	5.5	4.2	3.6	3.5	3.5	3.5

Some results found in the literature on the combustion of particles of aluminium and manganese in various gaseous mixtures at atmospheric pressure are collected in Table 24. The combustion time (calculated according to (42)) of drops of benzene in air is given as a comparison since no experimental data on the burning of liquid drops of diameter 10-50 microns were available.

The data of Refs. 59, 60, 62 for aluminium are in agreement but the combustion time of aluminium in Ref. 63 is considerably higher. There can be complications owing to the formation of hollow shells of Al_2O_3 around the aluminium particles (Fig. 16) thus protracting combustion. The conditions under which these shells are formed or are not formed, whether they are

TABLE 24
Some literature data on the duration of combustion of magnesium
and aluminium particles in various gas mixtures

Fuel	Composition of gas in the surrounding volume	$\tau \cdot 10^3, \text{ sec}$							Ref.
		$d = 10 \mu$	$d = 20 \mu$	$d = 30 \mu$	$d = 40 \mu$	$d = 50 \mu$	$d = 80 \mu$	$d = 120 \mu$	
Al	Combustion products of $\text{C}_3\text{H}_8\text{-O}_2\text{-N}_2$ mixture (contain 5.8% O_2 ; 18.1% H_2O)				10.5 ($d_0 = 35 \mu$)	19			62
	Combustion products of $\text{CO-O}_2\text{-N}_2$ mixture (contain 7.9% O_2 ; 0.5% H_2O)				6.6 ($d_0 = 35 \mu$)	12			62
	Combustion products of $\text{C}_3\text{H}_8\text{-O}_2\text{-N}_2$ mixture (contain 5.5% O_2 ; $T = 2510^\circ\text{K}$)		$d_0 = 23 \mu$			13			59
	Combustion products of $\text{CH}_4\text{-O}_2$ mixture	2-9	7-19	16-33	28-49	41-64			63
Mg	Air					1.85	6.2	16.8	64
	$20_2 + 8 \text{ Ar}$					1.75	5.85	15.8	64
	$20_2 + 8 \text{ He}$					1.3	4.3	11.5	64
C_6H_6	Air	0.078	0.31	0.7	1.24	1.94	5	11.2	

formed round all particles or only a certain fraction of them or whether they exist during the whole period of combustion of a particle, etc, are not yet established. Another complicating factor is the breakup of particles during combustion - by fragmentation, disruption, etc (see Fig.13 for aluminium and Fig.15 for titanium). This phenomenon is apparently connected with the accumulation of metal vapours under the oxide film and the subsequent sudden bursting of the latter. It is natural that when particle fragmentation occurs the time of combustion can be considerably decreased.

Magnesium particles ($d = 50 \mu$) burn considerably more rapidly than aluminium particles. It should be noted that in changing from air to a $2O_2 + 8He$ mixture (thus the volume percentage of oxygen remaining unchanged) the time of burning decreases considerably (about 1.5 times). This is in qualitative agreement with the theoretical expressions since the diffusion coefficient of oxygen in helium³⁴ is $0.638 \text{ cm}^2 \text{ sec}^{-1}$ and in air $0.178 \text{ cm}^2 \text{ sec}^{-1}$.

The combustion time (and hence the linear burning rate) of magnesium particles is of the same order as for organic fuels. Since r_p/r_d for magnesium is considerably less than for organic fuels because of the essentially higher heat of evaporation, 1260 cal/g for magnesium as against ~100 cal/g for the majority of hydrocarbon fuels, the burning rate of magnesium for unit surface of combustion front will be higher than for organic fuels.

So far only the case where the reaction takes place in a certain zone at a particular distance from the surface of the particle has been considered. However, there are two reaction zones during the burning of a small sphere of ammonium perchlorate in an atmosphere of fuel gas (see Refs.231, 232). The kinetically controlled flame of the NH_4ClO_4 decomposition products (see sections 10, 19) is located close to the surface of the small sphere and the diffusion flame is located further away. The combustion mechanism is complex (see section 10) and is, of course, not necessarily fitted by the simple diffusion theory. Nevertheless for the burning of NH_4ClO_4 in C_3H_8 and NH_3 the relationship (41) $d^2 = d_0^2 - nt$ appeared to be correct. However this result does not give any evidence for the diffusion character of the burning. Moreover, the form of the dependence $d(t)$ for the combustion of a small sphere of NH_4ClO_4 in an inert atmosphere is not certain; apart

³⁴On analogy with the combustion of gaseous mixtures it seems probable that there is an increase in burning rate as d decreases. It is not impossible that $d^2 = d_0^2 - nt$ may be obtained.

from this, in the present example functions have been discovered for the quantity n which are not characteristic of diffusion controlled combustion. Thus addition of 1% of copper chromite decreased n by approximately 1.5 times. With increase of pressure (from 1 to 5 atm) the value of n increased considerably ($n \propto p^{0.57}$). The effect of kinetic factors was also evident in that small spheres of $KClO_4$, NH_4NO_3 and KNO_3 , in contrast to NH_4ClO_4 , could not support stable combustion in an atmosphere of propane (for $p < 3$ atm). Furthermore it was shown that for NH_4ClO_4 , n increases with decrease in d_0 , although according to the theory $n \neq f(d_0)$.

The constant n increased slightly (and moreover linearly) with increase in the velocity of the gas ($n = n_0 + nV$). At 1 atm abs the value of n_0 in C_3H_8 was ≈ 0.036 cm²/sec and in NH_3 about 0.027 cm²/sec. For comparison the value of n_0 for the combustion of drops of kerosene in oxygen (0.01 to 0.015 cm²/sec) and of hydrazine in oxygen (0.035 cm²/sec) is given.

The results of experiments on the combustion of small spheres of NH_4ClO_4 in a mixture of H_2-N_2 are in disagreement with the diffusion theory to an even greater extent. In this case the relationship $d^3 = d_0^3 - kt$ was obtained, where k was almost independent of the hydrogen concentration.

C RATE OF PROPAGATION OF A FLAME IN SUSPENSIONS OF FUEL ATOMIZED IN AIR AND OXYGEN

In the combustion of atomized fuel the rate of burning (or the time of burning) of an individual particle is the basic parameter. However, in some problems the rate of propagation of the flame through a flow of suspended particles of fuel in a gaseous oxidizer is also of interest (see Refs. 77-79, etc).

O.I. Leipunskii⁶⁵ noted that the combustion of a suspension can be considered as the combustion of a homogeneous mixture, provided that the reaction in the combustion zone is subordinated to the mechanism characteristic of particle combustion. Later, this question is considered in more detail; here merely a few experimental results^{77,78} are given. Suspensions of aluminium powder in air ($\alpha = 3.15$ to 1.26) and of graphite powder in oxygen ($\alpha = 0.52$ to 0.46) were studied. In all cases the burning rate over the range of α investigated increased with increased concentration of fuel (Table 25).

TABLE 25

Linear and mass rates of flame propagation in suspensions
of aluminium in air⁷⁷
 (19 mm diameter bunsen burner)

C_A , mg litre ⁻¹	α	u, cm/sec		m, gm cm ⁻² sec ⁻¹	
		d < 10 μ	d < 30 μ	d < 10 μ	d < 30 μ
100	3.15	21	15	0.0275	0.0196
150	2.1	28.5	19	0.0387	0.0258
200	1.58	34.5	23	0.0486	0.0324
250	1.26	39.5	26	0.0577	0.038

At $\alpha = 1.26$ the mass burning rate of an aluminium-in-air suspension is of the same order as the mass burning rate of stoichiometric mixtures of saturated hydrocarbons. The flame velocity in graphite suspensions is significantly less than in aluminium suspensions.

Analysis of the experimental data is difficult since the flame velocity depends largely on the apparatus parameters, such as type and diameter of burner.

5 COMBUSTION DUE TO REACTION IN THE CONDENSED PHASE

In the combustion of condensed substances a regime can be established in which the main heat release, and in the limiting case of so-called 'flameless combustion' all the heat release, is evolved during reaction in the solid or liquid phases. Such a regime, from the theoretical point of view, should be sharply distinguished from the combustion of homogeneous gaseous and volatile systems, since in the condensed phase the rate of diffusion of the combustion products and, in particular, of active particles, in the unburnt substance is practically zero, and the propagation of combustion can proceed only as a result of heat transfer by thermal conductivity.

Further, it is natural to expect that the absolute value of the rate of combustion and its dependence on pressure, initial temperature, density, etc, for such a combustion regime will be significantly different from the analogous dependences for gaseous systems.

At first sight it might be expected that, for the regime where all the heat is evolved in the condensed phase, the absolute value of the rate of combustion would be very high, since the density of the condensed phase is

high, and also its thermal conductivity exceeds the thermal conductivity of the gas near the combustion front for volatile systems. It might also be expected that the rate of 'flameless' combustion would not depend on pressure and, in particular, should proceed steadily in a high vacuum. The mass rate of 'flameless' combustion should fall steeply on decrease of density of the system since the rate of reaction is decreased with fall of concentration of the unburnt substance. Finally, for those substances for which 'flameless' combustion is a regime with incomplete liberation of the heat of reaction and consequently a low temperature regime, there should be a high temperature coefficient.

No substance is described in the literature for which all the above predictions have been observed. However, substances which show clearly some of these predictions are not rare; the other predictions are absent in such cases or have not been investigated.

(1) A comparatively large group of fast-burning explosives is described in the literature. Data for some of these are given in Table 26.

TABLE 26

Linear and mass rates of burning of some fast-burning explosives at 1 atm

Substance	u , cm/sec	m , gm cm ⁻² sec ⁻¹	Ref.
Lead trinitroresorcinate (lead styphnate) $C_6H(NO_2)_3O \cdot Pb \cdot H_2O$	26-27	100	66
70% lead styphnate + 30% trinitro-triazido-benzene $C_6(NO_2)_3(N_3)_3$	26	-	67
40% lead styphnate + 60% talc	14.6	-	31
Diazodinitrophenol $C_6H_2(NO_2)_2ON_2$	2.15	3.12	31
Mercury fulminate $Hg(ONC)_2$	1.55	5.9	31
Potassium picrate $C_6H_2(NO_2)_3OK$	1.50	2.74	31
Tricycloacetone peroxide $C_3O_6(CH_3)_6$	0.95	1.16	31

Comparing Tables 26, 1 and 13 it is evident that at 1 atm the mass burning rate of explosives exceeds the burning rate of oxygen mixtures and volatile substances by an order of magnitude, and for lead styphnate by 2.5 orders of magnitude.

A second feature is also observed for lead styphnate, apart from its very high absolute rate of burning - that its burning rate is almost pressure independent. At a pressure of 15 mmHg⁶ in the bomb, $u \approx 25$ to 26 cm/sec, but at 50 atm the burning rate increases to 33 to 35 cm/sec and remains unchanged over the range 50 to 400 atm⁶⁶.

Fast-burning lead and potassium picrates also have a considerable range of pressure where the burning rate is practically independent of pressure. Thus for lead picrate the burning rate at 100 atm gauge is ~ 26 cm/sec and at 300 atm gauge ~ 31 cm/sec⁶⁶. For potassium picrate⁶⁹ the burning rate is practically constant at 10 to 80 atm and is ≈ 6 cm/sec. A more complicated dependence was obtained for potassium picrate in Ref. 70: the burning rate has a maximum ($u_{\max} \approx 6$ cm/sec) at 5 to 6 atm abs, then it decreases slowly to 4.3 cm/sec for an increase in pressure up to 25 atm abs and after that it remains constant in the range 25 to 125 atm abs.

However below a certain pressure the burning rate of lead and potassium picrates begins to fall rapidly and finally burning is extinguished (for potassium picrate at 500 mmHg and for lead picrate at 20 atm).

For mercury fulminate over the whole of the pressure range studied (10 mmHg to 150 atm) the burning rate increases with increase in pressure (at $p < 1$ atm abs u (cm/sec) = $0.4 + 1.1 p$ (atm abs) and at $p > 1$ atm abs $u \propto p^{0.5}$). It has been shown³¹ that at $p < 1$ atm abs the rate of burning increases with increase in pressure also for trinitrotriazidobenzene and tricycloacetone peroxide. The dependence of the mass rate of burning on the relative density $\delta = \rho/\rho_{\max}$ was studied for mercury fulminate. The mass burning rate immediately begins to rise with decrease in density, at first insignificantly and then very rapidly.

The temperature coefficient $\beta_u = d \ln u / dT_0$ for mercury fulminate is equal to $5.1 \cdot 10^{-3} \text{ deg}^{-1}$ (in the range 20 to 105°C)³¹, i.e. it has the same value as for liquid nitroesters (see Table 17).

⁶It is necessary to note that, from the laws of conservation of mass and momentum, the pressure at the combustion front for fast-burning substances can greatly exceed the pressure (p_∞) in the surrounding volume, and this effect becomes considerable at low p_∞ . Calculations⁶⁸ show that in the case of lead styphnate the pressure at the combustion front cannot be less than a few atmospheres.

(2) The regime of flameless combustion for ballistite powders was discovered and investigated in detail by P.F. Pokhil^{41,71}. Such a regime can be observed only in a vacuum for a comparatively narrow range of pressures and at a high initial temperature. Moreover combustion is flameless not only in the conventional sense, i.e. in the sense that the whole of the heat of reaction is emitted in the condensed phase, but also in the literal sense, since no luminosity is observed above the surface of the powder even in complete darkness. The rate of flameless combustion does not depend on pressure; at a sufficiently high pressure, a flame appears above the surface of the powder, and the rate of burning begins to increase with pressure (Table 27).

TABLE 27

Dependence of burning rate of pyroxylin powder on the pressure
in a nitrogen⁷¹ atmosphere

$$T_0 \approx 90^\circ\text{C}$$

p, mmHg	u, mm/sec	p, mmHg	u, mm/sec	p, mmHg	u, mm/sec	p, mmHg	u, mm/sec
1	0.8	18	0.8	120	1.1	550	2.4
2	0.8	30	0.8	200	1.4	680	2.7
5	0.8	70	1.0	280	1.6	720	2.8
9	0.8			410	2.0		

The temperature coefficient of the burning rate $\beta_u = d \ln u / dT_0$ for this combustion regime is high and amounts to $11.2 \cdot 10^{-3} \text{ deg}^{-1}$ for the range 90 to 140°C ⁷¹.

The independence of the burning rate on pressure for the flameless combustion regime was also observed for nitroglycerine powder (in the range 2 to 40 mmHg, when $u = \text{const} = 0.5 \text{ mm/sec}$).

It should be noted that the absolute magnitude of the rate of flameless burning for the given pressure range has to be considered as high, since at 20 mmHg the mass rate of burning of pyroxylin and nitroglycerine powders is 1 to 1.5 orders of magnitude higher than the mass burning rate of gaseous mixtures based on oxides of nitrogen⁶.

The data for gaseous mixtures refer to room temperature, but an increase of the initial temperature to $\approx 100^\circ\text{C}$ does not change the order of magnitude of the burning rate, since for gaseous mixtures $\beta_m = d \ln m / dT_0 \approx 10^{-3}$.

The mass burning rates m , $\text{gm cm}^{-2} \text{sec}^{-1}$ at 20 mmHg of pyroxylin and nitroglycerine powders ($T_0 \approx 100^\circ\text{C}$) and gaseous mixtures ($\alpha = 1$) based on oxides of nitrogen ($T_0 \approx 20^\circ\text{C}$)⁹ are given below:

Powder		Gaseous system	
Pyroxylin	0.128	$\text{C}_2\text{H}_2\text{-N}_2\text{O}$	0.0071
Nitroglycerine	0.080	$\text{H}_2\text{-N}_2\text{O}$	0.007
		$\text{C}_2\text{H}_2\text{-NO}_2$	0.0054
		$\text{H}_2\text{-NO}_2$	0.0047
		$\text{C}_2\text{H}_4\text{-N}_2\text{O}$	0.0043

Consequently at 2 mmHg this difference can increase further by about an order of magnitude.

On the other hand, the rate of 'ordinary' burning of a powder has the same order of magnitude as the (mass) burning rate of gaseous mixtures based on oxides of nitrogen. Thus at 1 atm abs and 18°C the burning rate of nitroglycerine powder⁷² is $0.08 \text{ gm cm}^{-2} \text{sec}^{-1}$, whereas the mass burning rate for mixtures based on NO (for various fuels) lies between the limits 0.02 to $0.106 \text{ gm cm}^{-2} \text{sec}^{-1}$ (see Table 2) and for mixtures based on NC_2 within the limits 0.035 to $0.226 \text{ gm cm}^{-2} \text{sec}^{-1}$, etc.

(3) For nitroglycerine powder at atmospheric pressure a rapid rise in the temperature coefficient of the burning rate with increase in initial temperature was observed⁷². The value of the temperature coefficient of the burning rate $\beta_u = d \ln u / dT_0$ for nitroglycerine powder (calorific value 870 cal/g) at atmospheric pressure is as follows:

Temperature, $^\circ\text{C}$	$\beta \cdot 10^3, \text{deg}^{-1}$	Temperature, $^\circ\text{C}$	$\beta \cdot 10^3, \text{deg}^{-1}$
-180 to -100	2.5	0 to 20	7
-100 to -40	2.2	20 to 40	10.3
-40 to 0	2.16	40 to 80	14
-10 to +10	4.6	80 to 100	15.4
		100 to 120	16.1

An analogous effect was also observed¹⁶¹ for powder N at 1 atm abs, but the value of β was somewhat lower (for $T_0 = -78$ to $+40^\circ\text{C}$, $\beta \approx 6 \cdot 10^{-3} \text{ deg}^{-1}$; at $T_0 = 40$ to 130°C , $\beta \approx 12 \cdot 10^{-3} \text{ deg}^{-1}$).

An increase in β with increase in T_0 for powder N was also observed⁷³ at high pressures (10, 20 and 50 atm).

The most evident explanation of this effect is that as T_0 increases the role of the reaction in the low-temperature zone, in particular in the condensed phase, increases* with increase of T_0 .

The absolute magnitude of the burning rate, in the range of T_0 studied, is still closer to the burning rate of volatile explosives.

(4) The mass rate of burning of pyroxylin decreases perceptibly with decrease in density (Table 28).

TABLE 28

Dependence of the mass burning rate m , $\text{gm cm}^{-2} \text{ sec}^{-1}$
of pyroxylin on density

Density, gm/cm^3	m , $\text{gm cm}^{-2} \text{ sec}^{-1}$		
	$p = 21 \text{ atm}$	$p = 26 \text{ atm}$	$p = 31 \text{ atm}$
0.8	1.21	-	-
1.0	1.29	1.44	1.53
1.3	1.35	1.66	1.78
1.5	1.63	1.77	1.98

The decrease of burning rate (with decrease in p) for pyroxylin is very much more pronounced than for volatile explosives, where it is associated with the decrease in heat release per unit volume and with the corresponding increase in the role of heat losses, see section 2,D.

*It is paradoxical, however, that for nitroglycerine powder studied in Ref.235 the temperature coefficient not only did not rise, but even considerably decreased with increase of T_0 (at $T_0 < 60^\circ\text{C}$, $\beta \approx 19 \cdot 10^{-3} \text{ deg}^{-1}$ and at $T_0 > 60^\circ\text{C}$, $\beta \approx 6 \cdot 10^{-3} \text{ deg}^{-1}$).

Thus experimental results show that under certain conditions it is possible to observe very clearly some features which are apparently characteristic of combustion resulting from a reaction in the condensed phase⁶. At the same time there are usually a number of complicating circumstances since in most cases the reaction in the condensed phase proceeds only partially.

The phenomenon of dispersion must also be considered. It was first discovered in the combustion of mercury fulminate in a vacuum⁷⁵. A thick deposit of a very fine powder of mercury fulminate contaminated with mercury appeared on the walls of the bell jar wherein burning took place. If this deposit is collected and pressed, then this mercury fulminate, which has already been burnt, burns in the same way as fresh mercury fulminate.

The phenomenon of dispersion was later investigated in detail by P.F. Pokhil in connection with the combustion of ballistite powders^{41,71}. Dispersion amounted to 70% of the original powder for combustion in a vacuum.

Attempts were made in a series of theoretical investigations to obtain an expression for the rate of burning resulting exclusively from a reaction in the condensed phase in the presence of dispersion, in which case the rate of burning, in principle, can depend on pressure. Two different methods of approach to the problem have been examined.

(1) It is assumed that the burning rate is determined by the rate of heat release within the boundary of the particles in the condensed phase not detached from the solid, assuming that a reaction in the dispersed particles and even more so a reaction in the flame does not affect the rate of burning. The mean density of the substance in the reaction zone is close to the density of the original charge. The temperature in the reaction zone is low and equal to T_g , the temperature at the surface of the charge. In this method of approach the burning velocity falls as the degree of dispersion η_d increases*. Unfortunately the mechanisms of dispersion have been little studied experimentally, therefore the theoretical expressions (see for example

*For powders the necessary condition for the appearance of such features is a sufficiently high initial temperature of the powder.

*In the theoretical investigation²⁰², some conclusions were reached concerning the exceptionally high rate of burning in the absence of dispersion and for pyroxylin powder an estimate was given of $u \approx 2500 \text{ mm/sec} \neq f(p)$. This conclusion has as yet no experimental confirmation since the experimental value of u for pyroxylin powder at 1 atm abs and 90°C is $\approx 3 \text{ mm/sec}$ ⁷¹.

Ref.202) in which the dependences $u(p)$, $u(T_0)$, etc, are expressed by means of the dependences $\eta_d(p)$, $\eta_d(T_0)$, etc, are not even in qualitative agreement with experiment.

The particular case where η_d is determined by the solubility of the gaseous intermediates in the liquid layer on the surface of the powder has been examined²¹⁵. Definite estimates and comparison with experiment are not made.

(2) It is assumed²³⁸ that the burning rate is determined by the rate of heat release in the dispersed particles or liquid films which form in the layer of foam. The mean density of the reacting layer is close to the density of the gas, but the temperature can considerably exceed T_g . If the velocity of the particles and that of the gas are equal, the dependence $u(p)$ is close to $u \propto \sqrt{p}$.

As yet little work has been done on comparing the single-stage models discussed with experiment. It is clear, however, that for the most interesting systems the combustion which is known to exist is a multistage process and cannot be described by means of such models*.

In the combustion of ballistite powders there are three zones of heat release. P.F. Pokhil distinguished the reaction zone of the condensed phase, the smoke zone and the flame zone (see Refs.41, 71, 204, 205 and others). In the American literature (see Refs.240-244 and others) the terms foam-, fizz- and flame-zone are used.

The mechanisms of multistage combustion have been investigated experimentally by analysing experimental data on the functions $u(p)$, $u(T_0)$, etc, and by measuring temperature profiles and gas composition and also the distance between the zones, etc (see Refs.41, 71, 102, 103, 106, 109, 130, 131, 169, 204-206, 242-248, etc).

At low pressures, for ballistite powders, reaction in the condensed phase is rate-controlling^{41,71,240}. At pressures of several tens of atmospheres the burning rate is apparently determined by the reaction in the smoke

*In particular for ballistite powders the experimental function $u(p)$ shows an increasing dependence on pressure at sufficiently high pressures²³⁹, whereas the theoretical function $u(p)$, owing to a decrease in the degree of dispersion, should reach saturation at high pressures.

zone^{645,240} and the flame has only an insignificant effect on the burning rate^{240,242,247}. However, it is thought^{240,242} that at sufficiently high pressures the flame zone begins to play the leading role.

In a series of theoretical investigations an attempt has been made to modify the solution of Zeldovich and Frank-Kamenetsky or other analogous solutions by means of successive transitions from one stage to the next, taking into account the heat release at the given stage and the flow of heat from the other stages. An examination has been made of the more particular problem where there is a single reaction zone and a fixed heat flow from outside (see Refs.203, 207-212, 240, 241 and others). However it has not yet been possible to find an expression which will give in an explicit form the dependence of the rate of multistage burning on the pressure, the initial temperature, etc, for a given kinetic reaction in each stage.

The only case that is really clear from the theoretical point of view is that in which one of the stages plays the leading role (see section 10,A). However, experimental methods which would enable us to establish the presence of only one leading stage of combustion have not yet been devised.

On the other hand experimental techniques can be successfully applied to the case where one of the zones has practically no effect on the burning rate, because it is located too far away from the surface of the charge and the other combustion zones, although the main part of the heat of reaction may be evolved in the zone concerned (see, for example, Ref.247). This case has drawn the attention of theoreticians to consider how such a zone is maintained at a fixed distance from the surface of the charge and is not carried away by the product gas stream. The most convincing explanation (see Refs.213, 214, 240, 260) is that in such a zone the spontaneous ignition of the intermediates formed in previous stages occurs and thus guarantees an automatic adjustment of the burning rate.

⁶With an increase in the degree of dispersion the rate of heat release can decrease in the condensed phase and increase in the smoke zone. However, the rate of burning can in principle decrease or increase. The double role of dispersion can also to some extent appear even in flameless combustion; in this case owing to a trivial effect: the detachment and transport of particles result in a discontinuity in the condensed phase. In this sense the burning velocity is the sum of the velocity of gasification and the velocity of dispersion²⁰².

CHAPTER II

BASIC PROCESSES DETERMINING THE BURNING RATE OF CONDENSED MIXTURES:

THEORY OF COMBUSTION OF CONDENSED MIXTURES

The combustion of mixtures of solid fuels and oxidizers is more complex than the other forms of combustion discussed above. In the general case it is a multidimensional, multistage process and depends on both kinetic and diffusion factors. The burning rate of condensed mixtures depends only on those processes which occur in a very narrow zone adjoining the unburnt mixture. It is only in the limiting case of sufficiently finely dispersed mixtures of volatile components that combustion proceeds in the purely kinetic regime and the combustion front becomes plane.

6 RATE OF MIXING OF FUEL AND OXIDIZER

In order that the components of a condensed mixture may react with one another, mixing must take place sufficiently rapidly in the preheating zone or the reaction zone.

A INFLUENCE OF THE AGGREGATE STATE ON CHARACTER AND RATE OF MIXING OF COMPONENTS

The aggregate state of the fuel and oxidizer in the preheating zone and reaction zone has a pronounced effect on the rate of mixing and the character of the mixing. If the unburnt mixture is a mixture of two solid components, then in the preheating zone and the reaction zone each component can either remain in the solid phase, or liquefy or vaporize. There are therefore six variants⁸¹

(1) $s + s$; (2) $s + l$; (3) $s + g$; (4) $l + l$; (5) $l + g$; (6) $g + g$.

The mixing of the components before the beginning of the reaction can take place only when the fuel and oxidizer (or their decomposition products) possess sufficient mutual solubility. This condition is almost always fulfilled in case (6) and hardly ever in cases (3) and (5), since the number of grams of gas which can be dissolved or absorbed in a gram of liquid or solid is extremely small in comparison with the usual weight relationships between the components in condensed mixtures.

Thus in case (6) $g + g$ and also in cases (1) $s + s$, (2) $s + l$ and (4) $l + l$ (for components with sufficiently high solubilities) mixing may

take place only partially, but for sufficiently finely divided mixtures completely, before the beginning of the reaction. On the other hand in cases (3) $s + g$ and (5) $l + g$, which correspond to the combustion of a suspension of volatile particles or drops in a stream of gas, mixing can take place only simultaneously with the reaction⁸¹. The state of aggregation of the components can also have a great effect on the rate of mixing and the width of the mixing zone. In cases (6) $g + g$, and also (1) $s + s$, (2) $s + l$ and (4) $l + l$ the width of the mixing zone in accordance with equation (17) is expressed by the proportional relationship

$$h_{\text{mix}} \propto km\bar{a}^2/C_{\infty} D$$

where m is the mass rate of burning. The state of aggregation affects the magnitude of $C_{\infty} D$, where C_{∞} is the concentration of the diffusing component at a great distance from the surface of contact of the components and D is the coefficient of diffusion. If the particle diameter of the components is not too large, mixing takes place by molecular diffusion. If the particle diameter is sufficiently large, convective mixing can also occur (see below).

B VALUE OF MOLECULAR DIFFUSION COEFFICIENT IN VARIOUS MEDIA

There are numerous data on the diffusion coefficient (especially for gases). However all the data for gases relate either to self diffusion or to diffusion in binary mixtures (or in air). For multicomponent mixtures (to which belong the products of combustion of any real system) there are no experimental data, nor any basic methods of calculating the diffusion coefficient. The majority of the experimental data for binary mixtures is for not very high temperatures*.

The diffusion coefficient in gases is usually obtained from the equation

$$D = D_0 \frac{p_0}{p} \left(\frac{T}{T_0} \right)^n, \quad (43)$$

*Results for the diffusion coefficient of some metal vapours in a flame at $T \approx 1400-1800^\circ\text{C}$ are given in Ref.88.

where D_0 is the diffusion coefficient in cm^2/sec at $p = 1\text{-atm abs}$ and $T_0 = 273^\circ\text{K}$. Depending on the nature of the mixture the value of D_0 can change by at least an order of magnitude. Mixtures with hydrogen are outstanding for their high values of D_0 . For saturated hydrocarbons D_0 decreases monotonically with increase in length of the hydrocarbon chain^{30,82,83}.

Gas (in a mixture with air)	H_2	CO_2	CH_4	C_2H_6	C_5H_{12}	$\text{C}_{10}\text{H}_{22}$
$D_0, \text{cm}^2/\text{sec}$ [30]	0.611	0.138 [82]	0.196	0.108	0.067	0.046 .

Equation (43) is empirical; the value of the exponent n is determined for a given mixture from the experimental points. Therefore equation (43) does not permit a reliable extrapolation to be made beyond the limits of the temperature interval investigated. For a reasonably wide range of temperature it is usually assumed that $n = \text{constant}$, where n lies within the limits 1.5 to 2.0 (see Refs.84, 30 and others). The value of n is frequently taken to be 1.75. However for a closer approximation to the experimental data n is temperature dependent. Thus in Ref.85 the coefficient of self diffusion of CO_2 in the interval 200 to 1700°K is taken to be $D(\text{cm}^2/\text{sec}) = 0.0967 (T/273)^n$, where $n = 1.81 + 0.035 (T/273)$.

The relationship $D \propto 1/p$ which follows from equation (43) shows a smaller dependence of D on p than is actually observed^{82,86,87}; thus for the system $\text{H}_2\text{-N}_2$ the following values were obtained⁸⁶:

p, atm	$pD, \text{atm cm}^2 \text{sec}^{-1}$		p, atm	$pD, \text{atm cm}^2 \text{sec}^{-1}$	
	$T = 273^\circ\text{K}$	$T = 473^\circ\text{K}$		$T = 273^\circ\text{K}$	$T = 473^\circ\text{K}$
1	0.708	1.86	100	0.570	1.425
50	0.570	1.44	200	0.562	1.474

In most papers the value of D is given without any indication of the concentration to which it refers. There is, however, a considerable dependence of D on concentration $D(c)$ ^{86,87}. Thus for example the following values were obtained for the mixture $\text{N}_2\text{-CO}_2$ at 301°K ⁸⁷:

Mixture	D, cm ² /sec	
	p = 6 atm	p = 2.4 atm
~0 N ₂ + ~1.0 CO ₂	0.027	0.005
0.5 N ₂ + 0.5 CO ₂	0.030	0.0065
0.75 N ₂ + 0.25 CO ₂	0.032	0.007

In this case D increases as the content of the lighter component increases, which seems natural.

For the diffusion coefficient in the liquid and solid phases the equation

$$D = D_* e^{-E/RT} \quad (44)$$

is used, where D_* denotes the coefficient of diffusion for $T \rightarrow \infty$ and E is the activation energy. The values of D_* and E are determined by the experimental points and show a much greater dependence on the nature of the substance than the values of D_0 and n in equation (43) for gas mixtures.

The diffusion coefficient in the liquid and solid phases depends on the concentration of the diffusing substance. In aqueous solutions the function $D(C)$ shows a weak and ill-defined dependence of D on C . With increase in concentration the diffusion coefficient can decrease, remain approximately constant or increase, depending on the nature of the substance⁸². There are also data on the dependence $D(C)$ for diffusion in alloys⁸². For the diffusion of aluminium and zinc in copper the diffusion coefficient increases rapidly with concentration:

C, atoms %	C _{Al} = 4	C _{Al} = 12	C _{Zn} = 4	C _{Zn} = 12
D, cm ² /sec (800°C)	4.24 · 10 ⁻¹⁰	2.64 · 10 ⁻⁹	3.72 · 10 ⁻¹⁰	3.33 · 10 ⁻⁹

The dependence of the coefficient of diffusion in the liquid and solid phases on pressure is evidently slight, as shown by the following values for the coefficient of self diffusion in liquid CO₂ (Ref.82):

p, atm	71	138	307
D, cm ² /sec	4.56 · 10 ⁻⁵	4.04 · 10 ⁻⁵	3.2 · 10 ⁻⁵

We have seen (see equation (17)) that the rate of mixing depends on the product $C_{\infty} D \propto \rho D$ (for a gas $C_{\infty} D \propto \rho D \propto (D_0 p_0 \mu / RT_0) (T/T_0)^{n-1} \neq f(p)$). The value of $C_{\infty} D$ for diffusion in the gaseous, liquid and solid phases can now be considered.

For binary gaseous mixtures the value of D_0 lies within the limits ~ 0.05 to $1 \text{ cm}^2/\text{sec}$. Taking $n = 1.75$ a reasonably reliable value at 1000°C is obtained for $D_1 \text{ atm abs} \approx 0.7$ to $15 \text{ cm}^2/\text{sec}$ and $\rho D = 3 \cdot 10^{-4}$ to $3 \cdot 10^{-3} \text{ gm cm}^{-1} \text{ sec}^{-1}$. At 2000°C only a rough value can be deduced because of the wide extrapolation. For $n = 1.75$, this gives $D_1 \text{ atm abs} = 2$ to $40 \text{ cm}^2/\text{sec}$; $\rho D \approx 5 \cdot 10^{-4}$ to $5 \cdot 10^{-3} \text{ gm cm}^{-1} \text{ sec}^{-1}$.

The evaluation of $C_{\infty} D$ for diffusion in the liquid and solid phases lies between much wider limits and is less reliable. Some data on the diffusion coefficient are given in Table 29.

There are also data for diffusion in solid and fused salts at $T < 400$ to 700°C ⁸².

For diffusion across oxide films the value of C_{∞} is limited by the solubility of the metal or oxygen in the oxide. For solid Cr_2O_3 at 1000°C $C_{\text{Cr}} < 10^{19} \text{ atom/cm}^3 \approx 10^{-3} \text{ gm/cm}^3$ (Ref.93).

TABLE 29
Range of values D (cm²/sec) for diffusion in liquid and solid phases

System	Temperature, °C	
	1000	2000
Fe → FeS (liq); Fe → Cu ₂ S (liq)[89] Si; Ti; V; Nb in liquid cast iron[90] Fe; Co; Ca; Si; Nb; V; Ti; Zr in melt of 45% CaO; 47% Al ₂ O ₃ ; 6% MgO; 2% B ₂ O ₃ [91] Fe; Ni; Ca; Si; Nb; V; O in melt of 45% CaO; 40% SiO ₂ ; 20% Al ₂ O ₃ [91,92]	6 · 10 ⁻¹³ to 3 · 10 ⁻⁴ (in most cases 10 ⁻⁹ to 10 ⁻⁵)	5 · 10 ⁻⁵ to 5 · 10 ⁻²
Cr → Cr ₂ O ₃ (solid)[93] O → UO ₂ (solid)[94] Al ₂ O ₃ (solid)[95] O → Ti; Zr; Nb; Ta (solid)[96]	5 · 10 ⁻²² to 4 · 10 ⁻⁷ (in most cases 10 ⁻⁹ to 10 ⁻⁷)	10 ⁻⁹ to 10 ⁻⁴ (in most cases 10 ⁻⁵ to 10 ⁻⁴)

Since, however, in most cases data on C_{∞} are not available the product $C_{\infty} D$ may be evaluated taking $C_{\infty} \approx 1 \text{ gm/cm}^3$ (Table 30).

TABLE 30

Range of values of $C_{\infty} D$ ($\text{gm cm}^{-1} \text{ sec}^{-1}$)

T, °C	Gas phase	Liquid phase	Solid phase
1000	$3 \cdot 10^{-4}$ to $3 \cdot 10^{-3}$	$6 \cdot 10^{-13}$ to $3 \cdot 10^{-4}$	$5 \cdot 10^{-22}$ to $4 \cdot 10^{-7}$
2000	$5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$	$5 \cdot 10^{-5}$ to $5 \cdot 10^{-2}$	10^{-9} to 10^{-4}

Thus for $T < 1000^{\circ}\text{C}$ the rate of mixing in the gas phase is considerably higher than in the liquid phase and even more so than in the solid phase. With increase in temperature this difference decreases, but nevertheless at 2000°C the rate of mixing in the gas is still several orders of magnitude higher than in the solid phase especially when the fact that C_{∞} in the solid phase can be small is considered. However, the molecular transport velocity in the fused state at 2000°C is of the same order as the transport velocity in the gas.

It should be remembered that, in addition to molecular diffusion in the gas phase, convective mixing of the components can also take place (see section 6,D). The transport velocity by convection in a melt can be considerably lower than in the gas because of the much higher viscosity of the melt. However for systems whose components fuse before vaporization, or vaporize with the formation of a liquid, the liquid layer may be sprayed with gas and a drop of the liquid (or dissolved) component can be transferred to the reaction zone.

C RATE OF VAPORIZATION OF FUELS AND OXIDIZERS

In so far as the state of aggregation of the components strongly affects their rate of mixing, the question of the rate of vaporization of the components becomes of interest.

During the burning of ordinary disordered mixtures where the oxidizer crystals alternate successively with layers of fuel, the preheating and vaporization of each particle occur in a non-stationary regime. The rate of vaporization $w = w(t)$ of the oxidizer crystals and fuel layers can be measured by means of high-speed cinematography. However for various reasons

this is a difficult operation since it is necessary to take the photograph with sufficient magnification and with very short exposure; photography is made more complicated by the presence of flames and smoke, and in a number of cases by the presence of a condensed residue on the burning surface and so on. It is therefore not surprising that even the best series of photographs of the burning surface allow only very limited deductions to be made.

The rate of non-stationary vaporization must depend to a great extent on the heat required for the preheating and vaporization of the particle. Moreover, if a kinetically controlled decomposition flame is located in the immediate proximity of the surface of a particle, then, considering the burning zone as a whole, the calculation of the heat of vaporization of particles must include the emission of heat in this flame. From this point of view, the vaporization of NH_4ClO_4 and NH_4NO_3 is an exothermal process^{97,118}, although vaporization at the surface of NH_4ClO_4 and NH_4NO_3 crystals takes place with the absorption of heat: $\text{NH}_4\text{ClO}_4(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HClO}_4(\text{g}) - 58 \text{ kcal/mole}$; $\text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HNO}_3(\text{g}) - 40.5 \text{ kcal/mole}$. On the other hand the vaporization of fuels requires considerable heat transfer from the combustion zone, since the heat of depolymerization of typical polymers is 10 to 25 kcal/mole (Table 31), and the heat of vaporization of the corresponding monomers is 5 to 10 kcal/mole¹¹⁹.

Comparative data on the rate of non-steady vaporization of various substances could obviously be obtained by determining the time of vaporization of a particle of a given size, which at the moment $t = 0$ is suddenly moved into a stream of gas at a given pressure and temperature. As the time of vaporization τ becomes shorter, the rate of vaporization $\bar{w} = d/2\tau$ becomes larger. However, such an experiment has not been carried out.

On account of the difficulties associated with the determination of the non-steady rate of vaporization, the relative ease of vaporization for various substances has been evaluated using data which were obtained during their slow thermal decomposition and also during the steady vaporization of sufficiently thick laminae of fuel or oxidizer (by the heat transfer from a hot-plate or a hot gas stream or during the combustion of a lamina of fuel in an oxidizing atmosphere, or during the combustion of a lamina of oxidizer in a fuel gas, and, in the case of NH_4ClO_4 and NH_4NO_3 , also in an inert atmosphere). Naturally the mechanisms of vaporization can differ considerably in changing from one system to another and can differ to an even greater extent from the mechanisms of non-steady vaporization during combustion.

TABLE 31

Heat of polymerization and products of decomposition of some polymers

Polymer	Heat of polymerization, kcal/mole	Products of decomposition
Polymethylmethacrylate	13 ^[95] 10-13 ^[249]	Monomer (95% ^[128] ; >90% ^[249])
Polyisobutylene	12.3-12.8 ^[99] 10 ^[249]	Monomer 20-50% ^[128,249] Dimer, trimer, tetramer ^[249]
Polystyrene	16.1-16.7 ^[99] 17 ^[249]	Monomer 30-65% ^[99] ; ~65% ^[249] ; Dimer, trimer, tetramer ^[249]
Polybutadiene ^[249]	17-20	Monomer 20-30%; higher molecular weight products
Polyethylene	22-25 ^[249]	Monomer (up to 1% ^[99,128,249]); higher molecular weight products ^[249]

In particular, it is necessary to consider the effect of pressure. In spite of the scantiness of experimental data, it may be deduced that pressure has no effect, or a very small effect, on the rate of vaporization during slow thermal decomposition and also during the vaporization of a fuel on a hot-plate or in a stream of hot inert gas (for $Re = \text{constant}$). Thus an increase of pressure of nitrogen from 1 atm to 100 atm at 260°C had practically no effect on, and at 230°C only insignificantly increased, the rate of thermal decomposition of NH_4ClO_4 ¹⁰¹. An increase in the pressure of nitrogen from 1 to 7 atm abs did not have any effect on the rate of pyrolysis on a hot-plate¹¹³. A similar result was obtained for the range 1 to 26 atm for pyrolysis of NH_4ClO_4 on a porous plate²³³; in the case of a solid plate the rate of pyrolysis increased with increase in pressure at the given temperature of the plate, but this effect results from experimental error²³³.

In the case of the diffusive burning of a polymer plate an increase in pressure can evidently increase the rate of vaporization considerably, although the way in which the surface temperature of the plate changes during this process was not examined. The results obtained by indirect means, such as the increase with increase in pressure of the rate of burning of a liquid

with a free surface (see section 3,B) and of the rate of burning of a drop (see section 4,B), and also the result obtained¹²⁴ for a plate of vinyl plastic in contact with a layer of KClO_4 (see section 18) confirm this. In the range 10 to 40 atm the relationship $w \propto p^{0.2}$ was found for the linear rate of pyrolysis w .

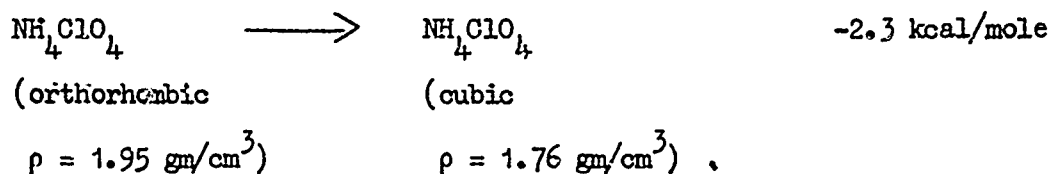
Finally for the combustion of NH_4ClO_4 and NH_4NO_3 , where a kinetically controlled decomposition flame is near the surface, the rate of vaporization $w = u$ depends to a great extent on pressure (see section 19). At the same time in the range of high pressures high values of w can be attained, thus for NH_4ClO_4 at 1000 atm $w = u \approx 40$ mm/sec was obtained¹²¹. Data on the dependence of the surface temperature T_s of burning strands on the pressure are ambiguous: an increase in the surface temperature with increase in pressure was observed for NH_4ClO_4 although the data are only reliable for low pressures, whereas for NH_4NO_3 , $T_s \neq f(p)$ (see below).

Other differences* in the mechanisms of vaporization also occur during slow thermal decomposition, in the stationary preheating wave and during the burning of actual mixtures. Nevertheless comparative data on the rate of vaporization during slow thermal decomposition and also in the stationary preheating wave are of great interest for the theory of combustion of systems of mixtures.

First we shall consider the slow decomposition of a weighed portion of substance, uniformly heated to a certain (not too high) temperature that is kept constant, or rises slowly with time. The rate of vaporization in this case is determined by the rate of evolution of gas, i.e. the number of grams of gas for 1 gram of the specimen in unit time. In practice arbitrary units are used: the time for decomposition of a given percentage of the substance at a given temperature; the temperature at which a given percentage is decomposed in a given time, etc.

*Thus for example in Ref. 113 it was shown that an addition of 3% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ increases the rate of slow thermal decomposition of NH_4NO_3 by several orders of magnitude and increases the burning rate of compositions based on NH_4NO_3 by approximately a factor of two, but has no effect at all on the rate of pyrolysis of NH_4NO_3 on a hot-plate. The increase in molecular weight of a polymer has a pronounced effect on its rate of vaporization on a heated plate, but has little effect on the burning rate.

The actual form of the kinetic curves (degree of decomposition v. time) can be very complex. It depends on temperature, on the presence of additives and impurities, the atmospheres in which the test⁶ was carried out, etc. In particular, the mechanism of decomposition of NH_4ClO_4 is much complicated by the presence at 240°C of the phase transition:



In addition, at $T \gtrsim 300^\circ\text{C}$ the decomposition of NH_4ClO_4 proceeds only partially, although the residue is identical with the initial NH_4ClO_4 (see, for example, Refs. 100 and 101, which contain a bibliography on this question).

Examination of the actual mechanisms of slow thermal decomposition would be beyond the scope of this book. Thus, only the respective data on the mean rates of vaporization of various substances will be examined. For polymers, there are similar data in Refs. 99, 128 and elsewhere. The relative order in which polymers increase in stability may depend on temperature (Fig. 17). However, many polymers can be listed unambiguously in accordance with their tendency to vaporization; polyformaldehyde vaporizes easiest of all, then polymethyl methacrylate, then polyisobutylene and polystyrene, etc. The most thermally stable is polytetrafluoroethylene (Teflon, Fluoroplast-4).

The mechanism of vaporization in a stationary preheating wave is now considered. In this case the rate of vaporization is determined as the linear velocity w of disappearance of the condensed phase at a definite value of the temperature T_s on the surface of a layer of component. In accordance with this definition, those substances vaporize more easily for which w is higher for a given T_s (or T_s is lower for a given w).

Initially, let us examine the data of vaporization in a flow of hot gas and during heating on a hot-plate. There is a large number of works dealing with ablation, i.e. the mass carried away in a flow of gas. Without attempting to summarize all of them, a few will be considered. The condition of interest to us is when ablation proceeds basically on account of vaporization.

The ablation of a series of homogeneous and reinforced plastics has been studied in a flow of the combustion products of the mixture $\text{C}_2\text{H}_2\text{-O}_2$ at $\sim 3000^\circ\text{C}$ and 1 atm abs¹¹⁰ or of air, heated in an arc discharge, in conditions when the

⁶Thus, for example, the presence of oxygen strongly modifies the mechanism of thermal decomposition of polymers (see e.g. Ref. 129). It makes a difference, also, whether the decomposition products are removed or accumulate in the vessel in which the experiment is made, in which case the ratio of the mass of the substance under investigation to the volume of the vessel is important.

enthalpy of air amounted to $6600 \text{ BTU/lb} \approx 3670 \text{ cal/gm}$, and the heat flow to the specimen was $1500 \text{ BTU ft}^{-2} \text{ sec}^{-1} \approx 360 \text{ cal cm}^{-2} \text{ sec}^{-1}$ (Ref.111). The rate of vaporization for teflon amounted to $0.45 \text{ mm/sec}^{110}$ or $0.89 \text{ mm/sec}^{111}$, and for nylon $0.51 \text{ mm/sec}^{110}$. The surface temperature reached 540°C for teflon¹¹⁰ or $< 520^\circ\text{C}^{111}$, and for nylon 1260°C^{111} .

Measurements of the rates of loss of weight \dot{M} (gm/sec) of a specimen ($\phi = 12.7 \text{ mm}$, $h = 25.4 \text{ mm}$) of plastic in a town gas-oxygen flame ($T \approx 2500\text{--}3000^\circ\text{C}$) have been made¹²⁵:

Nylon	0.180	Polyethylene	0.043
Polystyrene	0.052	Graphite	0.001 .
Perspex	0.045		

With nylon and to a lesser extent with polystyrene and polyethylene, drops of melted polymer were observed to be carried away by the flow. Consequently the quoted values do not allow the relative rates of vaporization to be assessed.

The rates of vaporization (w , mm/sec) of cylindrical specimens ($\phi = 10 \text{ mm}$, $h = 12 \text{ mm}$) of fuels in the flame of a charge ($\phi = 60 \text{ mm}$) of ballistite powder (at 1 atm abs) have been measured by the authors. The specimen was given an inhibitory coating on the longitudinal surface and was rotated on its axis at several revolutions per second to avoid asymmetry of combustion and trickling of liquid drops in the case of fuels which melt. The rate of vaporization (measured by the loss of weight during the experiment, which lasted for 20-30 seconds) was very small:

Polystyrene	0.015	Polyformaldehyde	0.030
Perspex	0.022	Urotropine	0.035 .

For urotropine the magnitude of w is evidently raised by the small crystals of urotropine cracking during rapid heating.

There is a series of works (Refs.112-116, 233, etc) in which the vaporization of specimens of perspex, NH_4ClO_4 , NH_4NO_3 and NH_4Cl pressed on to a hot-plate⁶ was studied (usually at 1 atm abs). The rate of vaporization is

⁶The vaporization of solid CO_2 on a hot-plate was studied in Ref.117.

measured by the displacement of the specimen. The temperature T_{pl} on the surface of the plate facing the specimens, or on the reverse side of the plate, is measured²³³ by means of thermocouples.

The magnitude of T_{pl} , with the corresponding correction or without correction, is assumed to be equal to the temperature T_s on the surface of the specimen. In pyrolysis experiments on a solid plate there is a gap between the specimen and the plate along which the products of vaporization flow out laterally. Consequently there is a temperature difference $\Delta T = T_{pl} - T_s$ between the plate and the specimen*. This gap can be reduced significantly if a porous plate is employed through which the vaporization products can be pumped away.

For substances capable of self-sustained combustion, e.g. NH_4ClO_4 , NH_4NO_3 , at sufficiently high T_{pl} there is a kinetic flame between the surface of the charge and the heated plate, and the regime of pyrolysis is completely changed. According to Ref.233, pyrolysis in the presence of burning can be studied only on a porous plate, since the scatter of the experimental points is very wide for a solid plate.

For all the cases studied, the experimental points plotted on $\ln w$, $1/T_s$ coordinates fall around a straight line, i.e. they satisfy the relationship

$$w = A e^{-E/2RT_s}$$

Values of A and E for some substances are given in Table 32. The data of the various authors differ widely.

Next let us consider vaporization during the diffusive combustion of a layer of fuel in a gaseous oxidizer. The burning out of a channel in a block of polymer with a given flow of oxygen through the channel (w_m was calculated from the loss of weight during the burning period τ) was investigated in Ref.122. For perspex at 1 atm abs $w_m \approx 0.1$ mm/sec, $T_s \approx 335-390^\circ C$, the magnitude of w_m falls with increase of τ . The incorporation in perspex

*An approximate estimate for $\Delta T = T_{pl} - T_s$ for the pyrolysis of perspex is quoted in Ref.114:

w , mm/sec	0.1	0.2	0.3	0.4	0.5
ΔT , $^\circ C$	6	14.5	25	40	60

TABLE 32
Rate of vaporization of different substances on hot-plates

Substance	Structure of plate	Constants in equation $w = Ae^{-E/2RT_s}$		Temperature, °C	Rate of vaporization w , mm/sec				Ref.
		A , mm/sec	E , kcal/mole		$T_s = 395^\circ\text{C}$	$T_s = 450^\circ\text{C}$	$T_s = 500^\circ\text{C}$	$T_s = 640^\circ\text{C}$	
Perspex	Fine wire	$1.88 \cdot 10^7$	55	450-503		0.1	0.3		112
	Solid	$3.8 \cdot 10^4$	37 24-25	440-575 395-640	0.043	0.087 (445°C)		0.54	113 114
NH_4ClO_4	Solid	$3.1 \cdot 10^2$ $58.8 \cdot T_s$	44 40	485-645			0.2 (510°C)	1.0 (630°C)	109 115
	Porous		32	400-640	0.02		0.1 (495°C)	0.5 (635°C)	116
			52* 20	< 475 > 475		0.0145	0.0645 (490°C)		233
NH_4NO_3	Solid	$1.2 \cdot 10^3$	14.2						113
NH_4Cl	Solid	23	20.4	300-600	0.01		0.03 (495°C)	0.075 (635°C)	112
	Porous		44	100-500	0.1 (370°C)		1.0 (495°C)		116

*Approximately the same value was obtained for a solid plate.

of 0.25 or 0.5% of carbon black, 30 or 60% of aluminium, or 30% of titanium hydride does not change the rate of vaporization. The magnitude of w_m for polyethylene is approximately the same as for perspex, but for polystyrene is significantly higher (on account of the trickling of liquid drops).

The burning rate of strips (1 in \times 6 in, thickness $\frac{1}{2}$ in) of butyl rubber, polyurethane rubber and copolymer of butadiene and acrylic acid has been measured²³⁴ in a stream of O_2 , F_2 and mixtures of O_2 - F_2 . The value of w for fluorine is higher than for oxygen, but approximately the same for the three polymers studied. For small rates of gas flow the value of w depends to a great extent on the flow rate and is almost independent of pressure (evidently the diffusion regime). On the other hand at high rates of gas flow the quantity w depends only slightly on the rate of flow but to a large extent on pressure, thus there is evidently a transition of combustion to the kinetic regime. In particular the following data were obtained for the burning of butyl rubber in oxygen and fluorine:

p, atm	w, mm/sec	
	in oxygen	in fluorine
1.75	0.155	0.34
4.2	0.28	0.66
8.4	0.42	0.90

Measurements have been made¹⁰² by means of infra-red spectroscopy on the value of T_s (in $^{\circ}C$) for the combustion of a series of polymers in air and oxygen:

Polymer	$T_s, ^{\circ}C$		Polymer	$T_s, ^{\circ}C$	
	in air	in oxygen		in air	in oxygen
Polyethylene	511	570	Polyurethane	burns badly	507
Polyisobutylene	428	469	Perspex	417	477-490

Vaporization during burning along the boundary between the layers of oxidizer and fuel was studied in Ref. 124. For the system of a layer of KClO_4 of thickness d between two thick plates of perspex, the burning rate of perspex near to the 'tip' of the flame was found to have the value $w = 0.264$ mm/sec for $d = 25$ mm and $w = 0.218$ mm/sec for $d = 3.8$ mm ($p = 1$ atm abs).

Finally, the combustion of NH_4ClO_4 and NH_4NO_3 in an inert atmosphere is examined. In this case vaporization takes place by the transfer of heat from the kinetic flame of $\text{NH}_3 + \text{HClO}_4$ or $\text{NH}_3 + \text{HNO}_3$. The burning rate of NH_4ClO_4 and NH_4NO_3 depends to a considerable extent on the pressure, the initial temperature, the presence of additives, density, etc, i.e. on the same parameters as the burning rate of homogeneous explosives, as may be expected since NH_4ClO_4 and NH_4NO_3 are weak explosives. In section 19 the functions $u(p)$, $u(T_0)$, etc, for NH_4ClO_4 will be studied in more detail, but here only data on the function for the surface temperature $T_s = f(u)$ will be given.

The value of the surface temperature for NH_4NO_3 with 2.5% additive was measured¹⁰⁸ using Pt-Pt/Rh thermocouples at different pressures. In the range 140-280 atm the surface temperature was practically independent of pressure (at 140 atm, $T_s = 325$ and 315°C ; at 210 atm, $T_s = 306, 317$ and 285°C ; at 280 atm $T_s = 313$ and 318°C). At the same time the burning rate increased considerably, i.e. from 4 mm/sec at 140 atm to 8 to 9 mm/sec at 280 atm. This result is in complete disagreement with the relationship $w = u = A e^{-E/2RT_s}$. Analogous results were obtained in this work for hydrazine nitrate and the eutectic mixture of ammonium and hydrazine nitrates.

For NH_4ClO_4 the value of T_s increases with increase of u , if u increases due to increase of pressure:

p , atm	10^6	21	35	70
T_s , $^\circ\text{C}$	490 ¹⁰²	~650 ¹³⁰	~680 ¹³⁰ ~800 ^{103, 104}	~720 ¹³⁰ ~990 ^{103, 104}
u , mm/sec			3-4	5-7

¹⁰⁸At room temperature pure NH_4ClO_4 burns only at $p > 20$ to 30 atm. In order to attain combustion at lower pressures, it was preheated or a fuel additive was introduced; the value of T_s in both cases was the same. In accordance with Refs. 102, 109, 130, the value of T_s for mixtures with volatile fuels was the same as for pure NH_4ClO_4 .

The values of T_s were measured by infra-red spectroscopy and appear to be reliable¹³⁰ only at $p < 4$ atm, since the mean temperature of a layer of thickness not less than 2μ is measured by this method.

If the burning rate was increased by addition of a catalyst¹⁰², then the value of T_s may not only not increase but even fall to a small extent. There are also other data that are not in agreement with the equation $u = Ae^{-E/RT_s}$. Thus the value of T_s , measured by means of thermocouples, falls¹⁰⁶ as the pressure increases from $\sim 420^\circ\text{C}$ at 50 atm to $\sim 330^\circ\text{C}$ at 100 atm, although the burning rate increases considerably. The value of T_s , measured for a series of compositions based on NH_4ClO_4 , remained constant¹³¹ within the limits of scatter, for changes in the burning rate produced by changes in pressure (in the range 1 to 15 atm), in the particle size of the oxidizer or by the addition of a catalyst*.

In concluding this section we can make the following deductions:

(1) In all the cases investigated the temperature on the surface of organic fuels and also oxidizers of the type NH_4ClO_4 , NH_4NO_3 , KClO_4 does not exceed 1000 to 1200°C and is usually 400 to 700°C . At the same time the combustion temperature of systems of mixtures usually lies within the limits 2000 to 3000°C (see for example Ref.126). Hence there is a reasonably wide temperature range within the limits of which the components (or decomposition products) are in the gaseous phase, and can mix thoroughly.

(2) At atmospheric pressure the rate of vaporization of organic fuels does not exceed 1 mm/sec both in case I, where vaporization takes place due to the conduction of heat from a hot-plate or flow of fuel gas, and in case II, where a lamina of fuel burns in a flow of gaseous oxidizer.

<u>Conditions for vaporization</u>	<u>Rate of vaporization w, mm/sec</u>
Burning of walls of conduit along which oxygen flows	0.1 to 0.4
Burning of lamina of fuel in contact with a lamina of oxidizer	0.2 to 0.3
Ablation in the combustion products of an oxygen flame or in a flow of gas heated in an arc discharge	up to 1.0
Vaporization on a hot-plate	up to 0.5

*Moreover, it is suggested¹³⁰ that the independence of the surface temperature of the burning rate¹³¹ and the fall in temperature of the surface with increase in burning rate¹⁰⁶ do not reflect the actual curve $T_s(u)$ and are connected with measurement errors, which become more significant as the burning rate becomes higher.

Evidently, however, with increase in pressure there should be a difference between cases I and II (see above).

(3) The function $w = Ae^{-E/2RT_s}$ is a good approximation to experimental data for pyrolysis on a hot-plate (but here the values of A and E measured by different authors for the same substance differ greatly). When combustion also occurs this relationship is not confirmed by experiment.

The so-called 'two-temperature theory of combustion' of Schultz and Dekker (see Ref.97) will be discussed briefly.

- (a) This theory starts from the relationship $w = Ae^{-E/2RT_s}$;
- (b) It assumes that the surface of the charge has a stable form;
- (c) It assumes that this surface consists of successive plane 'steps' of fuel and oxidizer.

For ordinary disordered systems supposition (a) has not been verified and suppositions (b) and (c) are known to be incorrect (combustion is unsteady and is multidimensional with respect to d, where d is the particle size of the components).

D CONVECTIVE MIXING IN GASEOUS PHASE

Up to this point it has been assumed that mixing of the components in the preheating zone and reaction zone proceeds exclusively as a result of molecular diffusion. However, it may be supposed that convective mixing can also play a definite role for mixtures with components which vaporize⁸⁰.

We may now consider the causes which can lead to the mutual penetration of volumes filled with the vaporization products of the components. The most important cause is the non-parallel flow of the vaporization products and also the difference in the absolute values of their flow velocities.

Experiments show that, at least when d is not too small, the surface of the condensed phase (c-phase) facing the flame is not plane (see Fig.18b) and wedge-shaped recesses, which increase as d increases, are formed along the edge of contact of the components. In the immediate vicinity of the c-phase surface the vaporization products move in a direction perpendicular to it because of the absence of any tangential forces. Therefore the direction of the velocity vector \vec{v} on the surface changes from point to point and near the surface the gas flows are in opposition, resulting in mixing.

From the law of conservation of mass flow for each of the components the absolute magnitudes of the velocity of the vaporisation products can be written

$$v_1 = \frac{\rho_1 w_1}{(\rho_1)_g}, \quad v_2 = \frac{\rho_2 w_2}{(\rho_2)_g} \quad (45)$$

where ρ , ρ_g are the densities of the condensed component and of its vaporization products, and w is the rate of vaporization (rate of disappearance of c-phase).

The mean values with respect to time \bar{w}_1 and \bar{w}_2 are proportional to one another and proportional to u , but the varying values w_1 and w_2 can be expressed for a given moment in time as an arbitrary ratio. Since ρ_1 and ρ_2 , $(\rho_1)_g$ and $(\rho_2)_g$ can also be expressed as an arbitrary ratio, then in general $v_1 \neq v_2$.

The inequality of the absolute values of the velocities of the vaporization products enables them to mix in a tangential (perpendicular to \vec{u}) direction and makes possible convective mixing in the axial (parallel to \vec{u}) direction. Consider the moment when, at a given point on the surface, component 2 is replaced by component 1. Since in general $v_{1a} \neq v_{2a}$ then either an elementary shock wave (for $v_{1a} > v_{2a}$), or an elementary rarefaction wave (for $v_{1a} < v_{2a}$), must proceed along the flow; these waves are reflected from the heterogeneities of density existing in the flow and from the surface of the c-phase and generate secondary, tertiary, etc, waves which gradually die away. Consequently, for example, for $v_{1a} > v_{2a}$ the stream of gas 1 will penetrate into the volume of gas 2 and the boundary between them will become diffuse owing to pulsations in the pressure and velocity of the gas, which arise during the passage of the elementary waves.

It is essential, however, to emphasize that the mixing of the gas in the axial direction plays an insignificant role in comparison with mixing in the tangential direction, since during the vaporization of a cube of solid component we obtain a square column of gas, the dimensions of the base of which do not change, whereas the height, and at the same time the mixing path in the axial direction, increase by ρ/ρ_g times, i.e. under ordinary conditions by 1 to 3 orders of magnitude.

The existence of turbulent mixing of the type considered is basically connected with the fact that the initial condensed mixture with its particles irregular in form and distribution has its own type of 'frozen' turbulence which 'comes to life' during the vaporization of the components. Hence there arises the question of artificially generated turbulence, similar to that which

occurs in the operation of various types of mixers, etc. This type of turbulence does not have any direct connection with the parameters (and in particular with the quantity Re) for steady flow of the vaporization and combustion products. The degree of artificially generated turbulence is greatest near the surface of the condensed phase (c-phase), i.e. precisely in that zone which usually has the greatest effect on the burning rate. Further along the flow the artificially created turbulence dies away. The basic scale of turbulence in the present case should be proportional to d .

For the artificially created turbulence under discussion we have at our disposal one parameter with dimensions of length d and one parameter with dimensions of velocity $\vec{v}_1 - \vec{v}_2$ from which we can form a combination with the dimensions of the coefficient of turbulent diffusion exchange (cm^2/sec):

$$D_{\text{turb}} \propto d(v_1 - v_2) \quad (46)$$

Thus $v_{1t} - v_{2t}$ is taken for mixing in the tangential direction and $v_{1a} - v_{2a}$ for mixing in the axial direction.

Substituting (45) in (46) and taking into account $\bar{w}_1 \propto \bar{w}_2 \propto u$ gives

$$D_{\text{turb}} \propto u d \rho / \rho_g \propto \frac{u d}{p} \quad (47)$$

It is now taken into account that the molecular diffusion depends on pressure, $D \propto 1/p$, but not on d and also that usually $u \propto p^\nu$ where $\nu > 0$. Hence it follows that the role of convective mixing becomes increasingly important with increase of d and p . It should also increase in proportion to the distortion of the c-phase surface, since in this way the angle of impact of the jet is increased and the path of mixing in the tangential direction is much shorter than in the axial direction.

Equation (47), of course, does not yet allow an assessment of the value of d at which convective mixing becomes comparable with molecular mixing, since expressions are lacking for the magnitude of the numerical proportionality constant on the right hand side of (47). In order to check qualitatively ideas put forward on the role of convective mixing the authors conducted experiments together with Yu. V. Frolov; using a ciné camera with a set of light-filters, we determined the height h of the inner cone of the flame of cylindrical charges ($\phi = 1 \text{ cm}$) of a mixture of KClO_4 - bitumen, with KClO_4 .

particle sizes of $d \approx 10, 180$ and 1700μ . The charge was burnt in a large vessel filled with nitrogen at a pressure of 1 atm abs and temperature 20°C . It was found that the height of the inner cone of the flame not only did not increase, but on the contrary decreased somewhat in changing from $d \approx 10 \mu$ to 1700μ , which supports the argument that there is an increase in the coefficient of mass transfer as d is increased.

The dependence $h(d)$ was also determined for the combustion of an individual 'particle'. For this purpose KClO_4 in the form of a powder was pressed into thick cylindrical tubes of perspex of different internal diameters (from 0.4 to 1.5 cm). It should be noted that in this case one has to reckon that $\phi = d$. From dimensional considerations

$$h \propto v d^2 / D \propto u d^2 / \rho_g D \quad (48)$$

and moreover for the system under investigation u is almost independent of d^{127} . Therefore for molecular mixing the relationship $h \propto d^2$ should be fulfilled. On the other hand if mixing is turbulent ($D_{\text{turb}} \propto d$), then $h \propto d$.

The experiments showed that in each the value of h varied perceptibly about some mean value from frame to frame. This mean value remained constant for a considerable part of the time of burning for $d = 4$ to 10 mm but for $d = 15 \text{ mm}$ it decreased as the burning of the charge proceeded. The following mean values h_m were obtained:

$d, \text{ mm}$	4	6	10	15
$h_m, \text{ mm}$	10	19	40	60

Using coordinates $(\log h_m, \log d)$ these points yielded a straight line corresponding to $h_m \propto d^{1.3}$, which is an argument in favour of the presence of convective mixing.

7 SOME MECHANISMS OF TRANSPORT OF PARTICLES AND DROPS BY A STREAM OF GAS

For most pyrotechnic mixtures the oxidizer vaporizes much more easily than the fuel. The fuel particles are entrained by the stream of vaporization products of the oxidizer and burn in a state of suspension above the surface of the charge. The transport of particles of fuel and oxidizer by a stream

of gas can occur also in systems with organic fuels. In addition to the particles of fuel and oxidizer there may be present in the flow particles of condensed residue formed during the decomposition of the initial components (e.g. KCl) or during their combustion (e.g. MgO , Al_2O_3 , etc).

There is a very extensive and varied literature devoted to the mechanisms of flow of two-phase media (solid particles - gas, or liquid drops - gas). However only a few elementary relationships for two-phase flow, useful for gaining an understanding of the processes which have an effect on the burning rate of condensed systems, are considered here. Hence the motion of particles is examined only in the vicinity of the surface of a charge and the flow of two-phase media through a nozzle, etc, is not discussed.

A THE LIMITING CASES OF EXTREMELY SMALL AND EXTREMELY LARGE PARTICLES

In order to understand the mechanisms of combustion of particles close to the surface of a charge it is useful to consider separately the cases of 'extremely small' and 'extremely large' particles.

The term 'extremely small' will denote a particle for which the time of flight until it acquires a velocity close to the velocity of the gas is much less than the time of stay in the zone which influences the burning rate (zone of influence).

The term 'extremely large' will denote a particle which is practically stationary relative to the charge or which moves with a velocity much less than that of the gas.

Using a system of coordinates referred to the combustion front and denoting the velocity of a particle by \dot{x} and the velocity of the gas by v , then within the limits of the zone of influence for an extremely small particle $\dot{x} \approx v$ and for an extremely large particle $\dot{x} \approx u$ where u is the burning rate.

To evaluate the sizes of the 'extremely small' and the 'extremely large' particle it is necessary to possess information in the first place on the size of the zone of influence and in the second place on the law of motion of a particle. The zone of influence is examined in more detail in section 10,B, but it should be noted here that quantitative information on the size of the zone of influence is extremely scanty. It is clear only that the width of the zone of influence does not exceed a few millimeters and decreases with increase in pressure. On the other hand, increase in particle size of the components evidently increases the width of the zone of influence.

The sizes of 'extremely small' and 'extremely large' particles can be evaluated for the particular case when:

- (1) There is a solitary particle which at the moment $t = 0$ is suddenly drawn into the flow of gas.
- (2) The force F_1 acting on the particle owing to the gas flow can be found by Stokes formula*.
- (3) The only other force acting on the particle in addition to F_1 is the force of gravity⁶. The usual experimental condition is that the charge burns from above downwards.

It should be noted that these limitations have no effect on the basic proposition concerning the presence of 'extremely small' and 'extremely large' particles (it is only the evaluations of the size of such particles that vary).

In this particular case the motion of a particle can be described by the equation

$$\frac{\pi}{6} d^3 \rho \ddot{x} = 3\pi \eta (v - \dot{x}) - \frac{\pi}{6} d^3 \rho g \quad (49)$$

where d , ρ are the diameter and density of the particles, η is the viscosity of the gas and g is the acceleration due to gravity.

Putting the right hand side of equation (49) equal to zero, the size of an 'extremely large' particle is obtained as

*In the general case the expression for F_1 is usually written in the form $F_1 = C_x \frac{1}{2} \rho_g (v - \dot{x})^2 \frac{\pi d^2}{4}$. For very small values of Re , where Stokes formula is valid, the dimensionless coefficient of friction is $C_x = 24/Re$. With increase in Re the experimental value of C_x becomes larger. (See for example Ref.32.)

Re	0.1	1.0	10	100
$C_x = 24/Re$	240	24	2.4	0.24
$(C_x)_{exp.}$	245	28	4.4	1.1

⁶Experimental data (mainly on the combustion of metal particles) confirms that there are evidently also forces of cohesion between a particle and the surface of the charge (if there is a molten layer, then the particle is held to the surface by forces of surface tension and viscosity). This problem has not yet been investigated.

$$d_* = \sqrt{\frac{18\eta(v-u)}{\rho g}} \quad (50)$$

Such an evaluation ($d > d_*$) is an upper limit, since particles somewhat smaller than d_* move so slowly that within the limits of the zone of influence their velocity in practice attains the value $\dot{x} \approx u$.

For $d < d_*$, integrating (49) for the initial conditions $x|_{t=0} = 0$ and $\dot{x}|_{t=0} = u$ yields

$$\dot{x} = u + \left(v - u - \frac{\rho d^2}{18\eta} g \right) (1 - e^{-18\eta t / \rho d^2}), \quad (51)$$

$$x = \left(v - \frac{\rho d^2}{18\eta} g \right) t - \frac{\rho d^2}{18\eta} \left(v - u - \frac{\rho d^2}{18\eta} g \right) (1 - e^{-18\eta t / \rho d^2}). \quad (52)$$

Putting $t \rightarrow \infty$ in (51) or making the right hand side of (49) equal to zero the value of the steady state velocity of the particle is obtained as

$$\dot{x}_* = v - \frac{\rho d^2}{18\eta} g. \quad \text{For very fine } (d \rightarrow 0) \text{ particles } \dot{x}_* \approx v.$$

From (51) and (52) the time t_k and length of path x_k which are necessary for the particle to acquire a velocity equal to $k \dot{x}_*$ (e.g. $0.9 \dot{x}_*$) are readily obtained. As an example, calculated for the vaporization products of an ordinary system of mixtures, using $u|_{1 \text{ atm abs}} = 1 \text{ mm/sec}$,

$$u|_{100 \text{ atm abs}} = 10 \text{ mm/sec}, T \approx 1000^\circ\text{C}, \mu = 40, \eta \approx 4 \cdot 10^{-4} \text{ gm cm}^{-1} \text{ sec}^{-1},$$

$\rho = 2 \text{ gm/cm}^3$, the distance in microns at which the particle succeeds in reaching a velocity $0.9 \dot{x}_*$ is

It should be noted that in Ref. 136 C_x was incorrectly assumed to be constant; this assumption is correct only for $Re \approx 2 \cdot 10^2 - 10^5$, but not for the small values of Re which are characteristic of the conditions of interest. As a result the values of x_k and t_k were very large.

d, micron	$x_k = 0.9$, microns		d, micron	$x_k = 0.9$, microns	
	p = 1 atm abs	p = 100 atm		p = 1 atm abs	p = 100 atm
0.1	0.16	0.016	10	1600	160
1	16	1.6	100	15.6 cm	-

Particles of size less than a micron can in practice be regarded as 'extremely small'. Particles of size $\sim 100 \mu$ and larger are 'extremely large'.

It is also of interest to evaluate the time of preheating t_h of the particle until it reaches the temperature of the gas. The value of t_h is limited by heat transfer from the gas to the particle. t_h is determined as follows: let at $t = 0$ a spherical particle with temperature T_s be drawn into the flow of gas with temperature T_g . For brevity, only the case is considered where the particle does not melt and does not evaporate to any significant extent at $T < T_g$ and where the temperature at various points on the particle changes in the same way with time. In addition t_h is equal to the time during which the difference in the temperature of the particle and the gas decreases by a factor e (from $T_g - T_s$ to $T_g - T_* = (T_g - T_s)/e$). The equation for the heat balance is

$$\pi d^2 \alpha' (T_g - T) \partial t = \frac{\pi}{6} d^3 \rho c \partial T \quad (53)$$

where α' is the coefficient of heat-transfer and c is the specific heat of the particle. Integrating (53) with the initial condition $T|_{t=0} = T_s$ yields

$$t = \frac{\rho c d}{6\alpha'} \ln \frac{T_g - T_s}{T_g - T} \quad (54)$$

For small spherical particles $\alpha' = Nu \frac{\lambda}{d} \approx \frac{2\lambda}{d}$.

Substituting in (54) this value of α' and also $T_g - T_* = (T_g - T_s)/e$, gives

$$t_h \approx \frac{\rho c d^2}{12 \lambda_g} = \frac{1}{12} \frac{d^2}{a} \frac{\lambda}{\lambda_g}, \quad (55)$$

where a is the temperature transfer coefficient (thermal diffusivity) of the gas, i.e. the time of heating of a small spherical particle ($Nu = 2$)⁶ is proportional to the square of its diameter, proportional to the ratio of the thermal conductivities of the particle and the gas* and inversely proportional to the temperature transfer coefficient of the gas.

The quantity t_h for small particles is readily evaluated numerically since the product ρc for inorganic salts, polymers and metals is in approximately the same range; thus for the substances of interest $\rho c = 0.3$ to $0.7 \text{ cal cm}^{-3} \text{ deg}^{-1}$, and at the same time ρc depends only slightly on the temperature. Taking $\lambda_g \approx (2 \text{ to } 4) \cdot 10^{-4} \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$ (see for example Ref.132), the following values are obtained for the time of heating of small particles, irrespective of whether fuel, oxidizer or metal:

d , micron	0.1	1	10
t_h , sec	$(0.6 \text{ to } 3) \cdot 10^{-8}$	$(0.6 \text{ to } 3) \cdot 10^{-6}$	$(0.6 \text{ to } 3) \cdot 10^{-4}$

The time of heating of a small particle is of the same order of magnitude as, or less by an order of magnitude than, the time of flight of a particle until it reaches a steady velocity.

⁶In Ref.133 the empirical equation for Nu in the case of a sphere surrounded by flowing gas is given by

$$Nu = 2 + 0.03 Pr^{0.33} Re^{0.54} + 0.35 Pr^{0.36} Re^{0.58}.$$

For $Re = 1$ (and $Pr \approx 1$) the value $Nu \approx 2.4$ is still closer to $Nu = 2$. In combustion conditions $Re < 1$ corresponds at 1 atm abs to particles less than $\sim 10 \mu$ and at 100 atm to particles less than $\sim 1 \mu$.

*Hence the time of heating of a particle, limited by heat transfer from the gas to the particle, exceeds the time of equalizing the temperature inside the particle (proportional to d^2/a) by λ/λ_g times; for example, by approximately three orders of magnitude for metal particles.

The time of heating of large particles (especially when the distribution of temperature inside the particle is taken into account) cannot be obtained by an elementary evaluation and it is beyond the scope of this work to examine this.

B PARAMETERS OF TWO-PHASE FLOW

It is of interest to obtain an expression for the number of particles and also the mass of particles and mass of gas in unit volume of two-phase flow and for their mean specific heat and mean thermal conductivity, etc; some of these expressions are given in Ref.134 and in another form in Ref.135.

For simplicity the system is considered in which the oxidizer vaporizes as a whole, but the fuel is non-volatile and burns in a stream of the vaporization products of the oxidizer. The following notation is used:

	Condensed mixture (c-phase)	Two-phase flow
Density, gm/cm^3		
oxidizer	ρ_{ox}	ρ_g
fuel	ρ	ρ
mean	$\bar{\rho}$	$\bar{\rho}'$
Fraction of fuel		
by weight, gm/gm	χ	χ'
by volume, cm^3/cm^3	V	V'
Fraction of area of cross-section occupied by fuel particles, cm^2/cm^2	S	S'
Number of particles of fuel in 1 cm^3	n	n'
Velocity (relative to combustion front), cm/sec		
of particles	u	\dot{x}
of gas	-	v
Specific heat, $\text{cal gm}^{-1} \text{ deg}^{-1}$		
oxidizer	c_{ox}	c_g
fuel	c	c
mean	\bar{c}	\bar{c}'
Thermal conductivity, $\text{cal cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$		
oxidizer	λ_{ox}	λ_g
fuel	λ	λ
mean	$\bar{\lambda}$	$\bar{\lambda}'$

All those quantities which refer to the c-phase will be regarded as constant, as will $\rho_g = p\mu/RT$ and \dot{x} , which will be considered only in the two limiting cases: for extremely large particles $\dot{x} = u$ and for extremely small particles $\dot{x} = v$. The expressions for $\bar{\rho}$, V , S and n are related to other parameters of the c-phase:

$$1/\bar{\rho} = \chi/\rho + (1 - \chi)/\rho_{ox} , \quad (56)$$

$$V = \bar{S} = \chi \bar{\rho}/\rho , \quad (57)$$

$$n = 6V/\pi d^3 = 6\bar{\rho}/\rho \pi d^3 . \quad (58)$$

Now consider the equation of conservation of mass flow for the state of flow where the fuel particles are accelerated by the gas and are heated but do not yet succeed in burning to any significant extent. In this case the conservation of mass flow of particles and mass flow of gas will be separately maintained:

$$\bar{\rho} \chi u = \rho S u = \bar{\rho}' \chi' \dot{x} = \rho S' \dot{x} , \quad (59)$$

$$\bar{\rho}(1 - \chi)u = \rho(1 - S)u = \bar{\rho}'(1 - \chi')v = \rho_g(1 - S')v . \quad (60)^*$$

From (59) and (60) we obtain

$$v' = S' = v \frac{u}{\dot{x}} = S \frac{u}{\dot{x}} , \quad (61)$$

$$n' = \frac{6V'}{\pi d^3} = n \frac{u}{\dot{x}} . \quad (62)$$

For large particles ($\dot{x} \approx u$) the fractions of the volume and of the area of cross-section of the flow occupied by the particles are equal to the corresponding quantities in the c-phase where the fuel particles form a stationary

*Note that in Ref.136 the left hand side of the equation (1') analogous to equation (60) is written inaccurately (it is valid only for $\dot{x} = v$ and $\rho = \bar{\rho}$).

lattice through which the gas flows. On the other hand for the case of small particles ($\dot{x} \approx v$) the fractions of the volume and of the area of cross-section of flow occupied by the particles is very much smaller than in the c-phase, since the same quantity of particles, which are confined in the c-phase in a cylinder of height u , are confined in a two-phase flow in a cylinder of height v , where $v \gg u$.

For the mean density of the substance (the number of grams of gas and particles in unit volume of flow) we obtain

$$\bar{\rho}' = \frac{\chi \bar{\rho} u}{\dot{x}} + \frac{(1 - \chi) \bar{\rho} u}{v} . \quad (63)$$

The first term on the right hand side of equation (63) corresponds to the mass of particles in unit volume of flow and the second term to the mass of gas in unit volume of flow. For large particles ($\dot{x} \approx u$) the first term, and consequently also $\bar{\rho}'$, is very large in comparison with the second, since the mass of large particles in unit volume of flow is the same as in unit volume of the c-phase. The second term in this case can be neglected ($u/v \ll 1$), so that $\bar{\rho}' \approx \chi \bar{\rho}$. In other words in this case the mass of particles in unit volume of flow is very large in comparison with the mass of gas in unit volume of flow.

For small particles ($\dot{x} \approx v$) equation (63) assumes the usual form

$$\bar{\rho}' v = \bar{\rho} u .$$

The ratio of the mass of small particles to the mass of gas

$$\frac{\chi \bar{\rho} u/v}{(1 - \chi) \bar{\rho} u/v} = \frac{\chi}{1 - \chi}$$

is the same as in the c-phase. This means that the mass of small particles in unit volume of flow is proportional to the density of the gas ρ_g and hence is proportional to the pressure.

It should be noted that for a given burning rate u and given density of gas ρ_g the velocity of the gas v in two-phase flow determined from (60)

$$\rho_g v = \rho u \left(\frac{1-S}{1-S'} \right) \quad (64)$$

will be lower than in single-phase flow, where it would be determined from the relationship

$$\rho_g v = \rho u .$$

In fact

$$\frac{1-S}{1-S'} = \frac{1-S}{1-S \frac{u}{\dot{x}}} < 1 ,$$

since $\dot{x} > u$. It is only for large particles where $S' = S$, that (64) gives the same value for v as (65). The meaning of this result is obvious; in two-phase flow the particles occupy a smaller fraction of the cross-section than in the c-phase, and the vaporizing component occupies a correspondingly larger fraction. In the limit, where $(1 - S \frac{u}{\dot{x}}) \rightarrow 1$, the velocity of gas in the two-phase flow is lower than in single-phase flow by $1 - S$ times.

The expression for the fraction by weight χ' of particles in two-phase flow, i.e. the mass of particles per unit mass of substance of the flow, is also useful:

$$\chi' = \frac{1}{1 + \frac{1-\chi}{\chi} \frac{\dot{x}}{v}} . \quad (66)$$

For small particles $\chi' = \chi$, i.e. the fraction by weight of small particles in two-phase flow is the same as in the c-phase. In the remaining cases $\chi' > \chi$. In particular for large particles $\chi' \rightarrow 1$. (These results for small and large particles were noted when studying equation (63).)

The specific heat for two-phase flow is equal to

$$\bar{c}' = \chi' c + (1 - \chi') c_g . \quad (67)$$

In the case of large particles ($\chi' \rightarrow 1$) the specific heat is practically equal to the specific heat of the particles $\bar{c}' \approx c$.

Only approximate formulae exist for the thermal conductivity of mixtures of two components. In particular Maxwell's formula can be used, which in the case of two-phase flow is written in the form

$$\bar{\lambda}' = \lambda_g \left(\frac{2\lambda_g(1 - V') + \lambda(1 + 2V')}{\lambda_g(2 + V') + \lambda(1 - V')} \right), \quad (68)$$

or the equation for the geometric mean value may be used:

$$\bar{\lambda}' = \lambda_g^{1-V'} \lambda^{V'}. \quad (69)$$

For small particles $V' \rightarrow 0$ and therefore $\bar{\lambda}' \approx \lambda_g$, i.e. the presence of small particles has almost no effect on the thermal conductivity.

Equations of type (68) and (69) can scarcely be used for large particles, since in this case the decisive role is played by heat exchange as a result of convection of the gas and radiation, which is not taken into account in these equations.

8 KINETIC AND DIFFUSION REGIMES OF COMBUSTION: SOME EXPRESSIONS FOR THE BURNING RATE

The rate of burning of condensed mixtures in the general case depends on kinetic and diffusion* factors. However there are some cases where only the kinetic or only the diffusion factors are decisive.

A KINETIC REGIME OF BURNING FOR EXTREMELY SMALL PARTICLES

If mixing is complete in the preheating zone, i.e. before the beginning of the reaction, then it has no effect on the burning rate. It is obvious that in this case combustion proceeds in the kinetic regime and the rate of burning does not depend on the particle size of the components and must be equal to the burning rate of the homogeneous system of that chemical composition. Such a regime of burning was first studied in Ref.127 and then more fully in Ref.81.

*Here and henceforth the term diffusion factors will be used to denote the factors associated with the rate of mixing of fuel and oxidizer and not those associated with the rate of diffusion of the products of combustion into the unburnt mixture (as was the case in section 1).

In section 6,A it has already been noted that mixing in the preheating zone can take place only if the fuel and oxidizer, or their decomposition products, possess sufficient mutual solubility and this condition is known to be valid for the system $g + g$ but not valid for the systems $g + s$ and $g + l$ (in the cases $s + s$, $s + l$, $l + l$ the possibility of the mixing of the components can be evaluated only for a particular system).

The regime under consideration can be observed only for sufficiently small values of d ($d \leq d_{\min}$). The quantity d_{\min} increases with increase in the rate of diffusion and has a lower limit, since it must in any case exceed the effective size of the molecules:

$$d_{\min} > 10^{-8} \text{ to } 10^{-7} \text{ cm} . \quad (70)$$

Hence the second condition for the existence of the regime under consideration is that the rate of inter-diffusion of the components must not be too small, thus satisfying condition (70).

Starting from the expressions given in Ref.127, the inter-diffusion of the components at a certain cross-section of the charge ($x = 0$) will be considered. After an interval of time ∂t the boundary of the mixing zone is shifted transversely by an amount of the order

$$\partial(y^2) \propto D \partial t . \quad (71)$$

Assuming that the combustion front moves relative to the given cross-section with a constant velocity u , we can write $x = x' - ut$ where x' is reckoned from the combustion front. Using the well known expression for the profile of the preheating wave in front of the combustion zone

$$x' = \frac{a}{u} \ln \frac{T - T_0}{T_c - T_0} \quad (72)$$

where a is the temperature transfer coefficient, cm^2/sec , and the temperatures T_0 and T_c refer respectively to the cold mixture and the reaction zone; putting $\partial t = \partial x'/u$ in (71) and integrating, the order of magnitude of d_{\min} is given as equal to

$$d_{\min} = \frac{1}{m} \sqrt{\frac{\bar{\lambda}}{\bar{c}}} \left[\int_{T_1}^{T_c} \frac{\rho D}{T - T_0} dT \right]^{\frac{1}{2}} \quad (73)$$

where m is the mass rate of burning (for $d < d_{\min}$), $\text{gm cm}^{-2} \text{sec}^{-1}$, ρ is the density, gm/cm^3 ; for the quantities $\bar{\lambda}$ ($\text{cal cm}^{-1} \text{sec}^{-1} \text{deg}^{-1}$) and \bar{c} ($\text{cal gm}^{-1} \text{deg}^{-1}$) the mean values over the preparatory zone are taken. If there are phase transitions in this zone, then it is divided into subzones and the integration in (73) is taken successively over each of them. For brevity it is assumed that mixing takes place basically in one subzone in the interval T_1 to T_0 (where $T_0 < T_1 < T_c$). The coefficient of interdiffusion of the gases is taken as $D = D_0 (T/T_0)^n$, where $n = 1.75$ to 2. For $n = 2$ we obtain from (73)

$$d_{\min} = \frac{1}{m} \sqrt{\frac{\bar{\lambda} \rho_c D_0}{\bar{c}}} \sqrt{\frac{T_c - T_1}{T_0} + \ln \frac{T_c - T_0}{T_1 - T_0}} \quad (74)$$

For diffusion in the solid and liquid phases $D = D_* e^{-Q/RT}$ and then (73) gives

$$d_{\min} = \frac{1}{m} \sqrt{\frac{\bar{\lambda} \bar{\rho}}{\bar{c}}} D_* \cdot \left\{ \text{li}(e^{-Q/RT_1}) - \text{li}(e^{-Q/RT_c}) + e^{-Q/RT_0} [\text{li}(e^{Q/RT_0} e^{-Q/RT_c}) - \text{li}(e^{Q/RT_0} e^{-Q/RT_1})] \right\}^{\frac{1}{2}}, \quad (75)$$

where $\text{li}(e^x)$ denotes $\int \frac{e^x}{x} dx$. The values $\text{li } z$ are taken from Tables, although for $Q \gg RT$ (for $e^{-Q/RT} < 10^{-4}$, $e^{Q/RT_0} e^{-Q/RT} > 10^4$) the approximation $\text{li } z \approx z/\ln z$ can be made with an error not greater than 10-12%. If in addition $e^{-Q/RT_c} \gg e^{-Q/RT_1}$, then (75) gives

$$d_{\min} = \frac{1}{m} \sqrt{\frac{\bar{\lambda} \bar{\rho}}{\bar{c}}} \sqrt{D_* \frac{RT_c}{Q} e^{-Q/RT_c}} \quad (76)$$

Equations (74) to (76) in principle allow evaluation of d_{\min} for any particular system.

It is of interest to evaluate the range of values of the quantity d_{\min} for a given type of system. This is particularly successful for the type $g + g$. In fact the value of the complex quantity $\theta = \sqrt{\frac{\lambda}{c}} \rho_0 D_0$ varies within relatively narrow limits for all gases which can appear as vaporization products of various condensed systems and for which Tables of data are available; thus the range $\theta = 10^{-4}$ to $10^{-3} \text{ gm cm}^{-1} \text{ sec}^{-1}$ includes all the ordinary di- and triatomic gases, the various gaseous hydrocarbons including the heaviest, the vapours of many organic liquids, etc (at temperatures from 200 to 300°C; it is assumed that $T_0 = 273^\circ\text{K}$). Apart from this, if the experimental dependence $m(p, T)$ is neglected, then the right hand side of equation (74) is independent of pressure and depends to a relatively small extent on the choice within reasonable limits of the temperatures T_c , T_1 and T_0 . Assuming for instance that the temperatures T_c and T_1 can change independently in the intervals 1500 to 3000 and 600 to 1000°K respectively, equation (74) gives the following range of values of d_{\min} :

$$d_{\min} \approx \frac{1.5 \text{ to } 35}{m} \text{ microns} \quad (77)$$

where m is in $\text{gm cm}^{-2} \text{ sec}^{-1}$. In Ref. 137 the experimental value d_{\min} for the stoichiometric mixture $\text{KClO}_4 + \text{bitumen}$ for $m \approx 0.2 \text{ gm cm}^{-2} \text{ sec}^{-1}$ was ~ 70 microns which lies within the limits of evaluation (77).

The position is much more difficult for the types $l + l$, $s + l$ and particularly for $s + s$, owing to the lack of data on diffusion in the systems, metal + salt, resins + salt, etc. Indirect data (diffusion of metals in metals and slags, mutual diffusion of salts, etc) show that for the system $s + s$ the diffusion coefficient depends to an extraordinarily large extent on the nature of the components and this excludes the possibility of any evaluation of d_{\min} from indirect data. For diffusion in the liquid phase the dependence on the nature of the components is considerably less but the range of d_{\min} , obtained from indirect data inserted in expression (75) (for reasonable assumptions regarding the range of variation of T_1 and T_c), extends over about four orders of magnitude. Such a wide evaluation has no practical interest.

B DIFFUSION REGIME OF COMBUSTION OF SUSPENSIONS OF SOLID PARTICLES

In the previous section 8,A it was stated that in systems of the type $g + s$ or $g + l$ a kinetic regime that is associated with the mixing of the components in the preheating zone cannot exist and that for these systems mixing can occur only simultaneously with burning.

However for mixtures $s + g$ or $l + g$ there can occur a pure diffusion regime (and in principle also a pure kinetic regime) associated with the fact that the combustion of each particle (or drop) takes place in a diffusion (or kinetic) region.

Only the diffusion regime is examined here, since the kinetic regime is clearly not experimentally attainable.

O.I. Leipunskii⁶⁵ suggested that the combustion of a suspension of solid particles could be treated in the same way as the combustion of a homogeneous gas mixture and in accordance with the theory of Zeldovich it was assumed that

$$m \propto \sqrt{\phi} \quad (78)$$

where m is the mass burning rate, $\text{gm cm}^{-2} \text{sec}^{-1}$, and ϕ is the rate of heat release in unit volume of two-phase flow (solid particles + gas), $\text{cal cm}^{-3} \text{sec}^{-1}$.

This supposition is true for extremely small particles, and it is this case which is studied in Ref.65. For large particles it is doubtful whether equation (78) can be applied, but nevertheless since there is a lack of more fundamental relationships this equation has to be used for qualitative deductions.

The heat release due to the combustion of particles can be written in the form (see Ref.138)

$$\phi = \rho \frac{\partial r}{\partial t} \pi d^2 n' Q \quad (79)$$

where ρ is the density of a particle, gm/cm^3 , $\partial r/\partial t$ is its burning rate, cm/sec , $2r = d$ is the diameter of a particle, cm , n' is the number of particles in 1 cm^3 of two-phase flow and Q is the heat of combustion for 1 gm of fuel, cal/gm .

Substituting $\frac{\partial x}{\partial t} = \frac{1}{r_p} (N + L)$ from (39) and n' from (62) in (79) the mass rate of propagation of flame is obtained:

$$m \propto \frac{1}{d} \sqrt{12 (N + L) Q \chi \frac{\bar{p}}{\rho} \frac{u}{x}} \quad (80)$$

If the dependence of the rate of burning on only the pressure and particle size is required, then (80) can be rewritten as

$$m \propto \frac{1}{d} \sqrt{\frac{u}{x}} \quad (81)$$

since all the remaining quantities under the square root in (80) are independent of pressure (N , Q , χ , \bar{p} , ρ) or almost independent of pressure (L).

For small particles $\dot{x} \approx v \propto pu/\rho_g$ and correspondingly $u/\dot{x} \propto \rho_g \propto p$. Thus for the rate of propagation of a flame in a suspension of small solid particles (or liquid drops) in the case where the particle combustion takes place in the diffusion regime

$$m \propto \sqrt{p/d} \quad (82)$$

(which is the same as equation (4) in Ref.65).

For large particles burning in the diffusion regime it follows from (81) that

$$m \propto 1/d \mp f(p) \quad (83)$$

Hence the velocity of propagation of a flame in a suspension of solid particles for the case of small particles depends on pressure and for the case of large particles is independent of pressure. However the rate of burning and time of burning of each individual particle (whether small or large) in the diffusion regime do not depend on pressure (see section 4.4). At the same time the number of small particles in unit volume of flow is proportional to the pressure, but the number of large particles in unit volume of flow is

independent of pressure (see equation (62)). Thus $m \propto \sqrt{p}$ for a suspension of small particles and $m \neq f(p)$ for a suspension of large particles.

In the derivation of (80) and (81) no assumption was made whether the particles were volatile or involatile since the mechanism of diffusive burning does not depend on volatility, which only changes the ratio r_ϕ/r_k and correspondingly the absolute magnitude of the burning rate; see section 4.A. However the experimental results quoted in chapter III show that for mixtures with components that are easily vaporized (to which belong such oxidizers as NH_4ClO_4 , KClO_4 , NH_4NO_3 and most organic fuels) u depends only to a slight extent on d and does not show the relationship $u \propto m \propto 1/d$.

It is only for involatile fuels (for example, graphite and tungsten) that u depends to a considerable extent on d and approaches the relationship $u \propto m \propto 1/d$ (see section 13).

In addition to the relationship $u(d)$ it is necessary also to consider whether the theoretical relationship $u(p)$ is in agreement with experiment. In accordance with equations (82) and (83) there should be a smaller dependence of u on p in the transition from small to large particles. However in Ref. 139 for the mixtures $\text{Al-Fe}_2\text{O}_3$ and W-KClO_4 the opposite effect was discovered: the burning rate for coarsely dispersed mixtures depended to a greater extent on pressure than for finely dispersed mixtures (see Table 41).

This discrepancy may be connected with the fact that combustion of the particles does not necessarily take place in a free gas flow. Hence the theoretical dependence $u(p)$ described by equations (82) and (83) is not the only possible one for diffusive burning.

The case where vaporization of the oxidizer is accompanied by the formation of a condensed residue (for example, $\text{KClO}_4 \rightarrow \text{KCl} + 2\text{O}_2$ or $\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + 1.5\text{O}_2$) or where part of the products of combustion at the combustion temperature is solid or liquid is considered in Ref. 140. In this case the condensed residue prevents the particles of fuel from being carried away by the gas and forms a more or less dense film through which bubbles and streams of gas burst.

In the present case the particles (both small and large) are stationary relative to the unburnt substance $\dot{x} \approx u$. Correspondingly the number of particles in unit volume of flow is constant for all pressures and is equal to the number of particles in unit volume of the initial mixture. However the magnitude of N from (80) may, generally speaking, depend on the

pressure, since diffusion does not necessarily take place in a free gas flow. In the general case $N \propto C_{\infty} D$, where D is the coefficient of diffusion, C_{∞} is the concentration of oxidizer at a great distance from the surface of the particle; for diffusion in a gas $D \propto 1/p$; $C_{\infty} \propto p$ and correspondingly $N \propto f(p)$, thus for the burning rate⁶

$$m \propto \frac{1}{d} \sqrt{D C_{\infty}} \quad (84)$$

A few particular cases will be considered:

(1) Molecules of oxidizer (for example $KClO_4$), without decomposing, diffuse through a film of condensed residue (for example KCl). For this case $C_{\infty} \propto f(p)$ and $D \propto f(p)$. Hence

$$m \propto 1/d \propto f(p) \text{ for any value of } d. \quad (85)$$

(2) Molecules of oxidizer decompose with the emission of oxygen, which diffuses through the film of liquid residue in the form of bubbles or in solution. In the latter case $C_{\infty} \propto p$ (according to Henry's law); the diffusion coefficient D , to a first approximation, does not depend on p . Hence

$$m \propto \frac{\sqrt{p}}{d} \text{ for any value of } d. \quad (86)$$

In practice, an intermediate case may occur: for extremely small values of d , where the surface of the components is very large, the oxidizer

⁴The case of involatile particles, for which only the diffusion regime of burning is observed, is being considered here; consequently $r_{\phi}/r_k \approx 1$ and $L \ll N$, thus $N + L \approx N$ (see expression (40)).

*The diffusion coefficient in solutions depends on the concentration of dissolved substance, but this dependence is relatively slight, moreover with increase in concentration there is observed not only a decrease but also an increase in D (see section 6,B).

succeeds in diffusing to the surface of a fuel particle* which has not yet decomposed, i.e. case (1) occurs and $m \neq f(p)$. However for large values of d , and considerable thickness of oxidizer, the overwhelming majority of oxidizer molecules decomposes first and then oxygen diffuses to the surface of the fuel particles. If under these conditions case (2) occurs, then for large particles $m \propto \sqrt{p}$.

A similar explanation is in agreement with the fact that for mixtures of $KClO_4$ with coarse particles of tungsten u depends on p to a less extent as the content of $KClO_4$ is reduced¹³⁹ (since in this case the thickness of the layers of liquid residue decreases and correspondingly the role of diffusion through the liquid is reduced). In addition, it was found¹³⁹ that u increasingly depends on p not only with increase in the particle size of the metal d_m , but with increase in the particle size of the oxidizer d_{ox} (for d_m constant). This result can be readily understood from the consideration that with increase of d_{ox} the path of diffusion of oxygen through the condensed residue increases in length.

C EXPRESSION FOR BURNING RATE WHEN HOMOGENEOUS AND HETEROGENEOUS REACTIONS OCCUR SIMULTANEOUSLY

In section 8,A the case where burning takes place as a result of a homogeneous reaction was examined, since mixing of the components is brought to completion in the preheating zone. On the other hand in section 8,B the case was examined where burning takes place as a result of a reaction near to the surface of the particles. In the present section the heterogeneous reaction is considered initially.

There is also the possibility that a homogeneous reaction in the mixture of the vaporization products might occur simultaneously with a heterogeneous reaction at the particles (see Ref.174). Moreover particles may be introduced into the system intentionally (catalytic or energy-providing additives), or they may appear spontaneously in the process of combustion (for example, soot).

Let the burning rate of a system without particles in the reaction zone be u and the burning rate of a system with added particles be u' . Their ratio is denoted by $u'/u = Z$.

*The practical problem is more complex since the combustion temperature of the particle is high and there is a gas film between the surface of the particle and the layer of condensed residue.

If the combustion of the system without added particles takes place in a regime close to the kinetic regime, then the burning rate is proportional to the square root of the rate of heat release in unit volume, ϕ_{hom} , as a result of homogeneous reaction (see Refs.26, 27), i.e.

$$u \propto \sqrt{\phi_{\text{hom}}} \propto \sqrt{p^{2\nu} e^{-E/RT_c}} \quad (87)$$

where p is the pressure, ν is the exponent in the equation $u = bp^\nu$, E is the activation energy, and T_c is the combustion temperature of the system without added particles.

When particles are introduced there is heat release as result of heterogeneous reaction at the surface (or close to the surface) of the particles. Where a homogeneous and heterogeneous reaction occur in the same zone,

$$u' \propto \sqrt{\phi_{\text{hom}}' + \phi_{\text{het}}} \propto \sqrt{p^{2\nu} e^{-E/RT_c'} + \phi_{\text{het}}} \quad (88)$$

where T_c' is the combustion temperature when particles are present.

Consider the case when the heterogeneous reaction takes place in the diffusion regime, i.e. its rate is limited by the velocity of approach of the reagents to the surface of the particles; then

$$\phi_{\text{het}} \propto (\rho_g D/d^2)(u'/\dot{x}) \quad (89)$$

where ρ_g is the density of the gas, D is the diffusion coefficient, d the size of the particles, and \dot{x} is the velocity of the particles.

For small particles \dot{x} is close to the velocity of the gas, and $v \propto pu'/\rho_g$ (where p is the density of the initial system). In this case

$$\phi_{\text{het}} \propto p/d^2 \quad (90)$$

Substituting (90) in (88), for the value of $Z = u'/u$ is obtained

$$Z \propto \left[\exp \frac{E}{R} \left(\frac{1}{T_c} - \frac{1}{T_c'} \right) + p^{1-2\nu} \frac{A'}{d^2} \exp E/RT_c \right]^{\frac{1}{2}}. \quad (91)$$

If T_c' is independent of pressure, i.e. if the intensity of burning of the particles is constant or the heat required to heat them is constant, then (91) yields the relationship

$$Z \propto \sqrt{A + Bp^{1-2\nu}}. \quad (92)$$

Hence, if for the system without added particles exponent $\nu < 0.5$, then the quantity Z increases with pressure, but if $\nu > 0.5$, then the quantity Z falls with pressure.

It is also evident from (91) that Z increases with reduction of particle size d , with increase of T_c' and with decrease of T_c . The latter denotes that, other conditions being equal, it is easier to increase the burning rate of a cool mixture, i.e. a mixture with a low combustion temperature.

In the literature there are a few experimental results which enable the validity of formula (92) to be assessed. The change in the burning rate of the stoichiometric mixture $KClO_4$ + bitumen ($\nu \approx 0.73$ in the range 5 to 100 atm) with the addition of particles of tungsten and other substances was investigated in Ref.138. In all cases the value of Z fell with increase in pressure, which is in agreement with (92).

The action of added particles of charcoal on the burning of PETN ($\nu \approx 0.95$) was investigated in Ref.201. In this case also the value of Z falls with increase of p and at the same time the exponent ν decreases to $\nu' = 0.6$ to 0.65.

It was shown by S.A. Tsyanov¹⁷⁴ that, for the gclatinized mixture NH_4ClO_4 ($\sim 5 \mu$) + perspex with $\alpha = 0.6$, u depends only very slightly on p :

p , atm	25	40	70	100
u , mm/sec	9.3	9.3	8.0	8.3

($\nu_{25-40 \text{ atm}} \approx 0$, $\nu_{40-100 \text{ atm}} < 0$); with the addition of charcoal or Cu_2O u depends more strongly on p . Consequently the value of Z rises rapidly with increase in pressure:

p, atm	Z		p, atm	Z	
	2% charcoal	2% Cu ₂ O		2% charcoal	2% Cu ₂ O
25	1.04	1.26	70	1.45	2.25
40	1.19	1.59	100	-	2.65

An increase in the exponent ν with the addition of soot was observed in Ref. 141 for the mixture NH_4ClO_4 -paraformaldehyde in the pressure range where $\nu = 0$ for the original system.

Thus the relationship (92) is in agreement with the experimental data to be found in the literature.

D THEORETICAL STUDY OF FLAME PROPAGATION ALONG THE CONTACT SURFACE BETWEEN FUEL AND OXIDIZER

The propagation of a flame along a plane and cylindrical contact surface between fuel and oxidizer was investigated experimentally^{124,127,166} and then theoretically¹⁴²⁻¹⁴⁵ as the limiting case of the combustion of a system with very large particle sizes of the components. However the combustion of ordinary composite mixtures not only leads to the propagation of a flame along the surface of contact of the components, but also involves the process of the transmission of burning from one particle of oxidizer to another through the layer of fuel owing to the transfer of heat from the neighbouring particles of the system¹²⁴.

Experimental work on the propagation of a flame along the surface of contact of the components will be considered later (section 18). At present only the deductions of the theoretical work are discussed briefly.

In Ref. 142, using the method of Zeldovich-Schwab, the two-dimensional problem of the combustion of plane layers of fuel and oxidizer was investigated using the assumption that the masses of oxidizer and fuel are in stoichiometric proportions, that the surface of the charge facing the flame is plane, etc. The solution is extremely cumbersome; at the same time an expression for the burning rate has not been obtained in an explicit form and the results of numerical calculation are not given.

It is suggested that the rate of burning u is practically independent of pressure. In section 18 it will be shown that this result contradicts

experiment* in almost all cases. The problem of the propagation of a flame along the surface of contact of the components was solved in Ref.143 using similar assumptions. The results of the solution are also similar; for instance it was found¹⁴³ that for the diffusion regime $u \propto 1/h \neq f(p)$, where $2h$, the width of the layer, is the same for the layer of fuel and the layer of oxidizer. The method of solution used was different from that in Ref.142.

The combustion of an ordered system has been examined¹⁴⁵ on the basis of the concepts of the 'two-temperature theory', which proposes that on the surface of the charge there are plane recesses and projections; the first correspond to the component that vaporizes more readily and the second to the component that vaporizes less readily. The expression for the burning rate was not deduced in an explicit form. The numerical calculation was given for the systems NH_4ClO_4 - polystyrene and NH_4ClO_4 - polyurethane, using data on the rate of pyrolysis on a hot-plate.

The results are given in the form of graphs on $\log u$, $\log d$ coordinates. For the system NH_4ClO_4 - polystyrene with oxidizer fuel ratios 90:10 and 80:20 calculation gives straight lines corresponding to the relationship $u \propto d^{-n}$, where $n \approx 0.9$ for any value of d . This result obviously contradicts experiment. The actual dependence of u on d is generally less and moreover the slope of the curve $u(d)$ (and consequently the value of the derivative $\partial \ln u / \partial \ln d$) changes as d changes. For the system NH_4ClO_4 + polyurethane (for oxidizer fuel ratios 90:10 and 80:20) the slope of the theoretical curve (coordinates $\log u$, $\log d$) increases with increases in d , i.e. the dependence of u on d becomes greater as d increases. This result is also doubtful. The mean value of the exponent n over the appropriate range of d in the theoretical relationship $u \propto d^{-n}$ for the system NH_4ClO_4 - polyurethane lies between 0.5 and 0.6, i.e. the theoretical dependence of u on d is too high in this case also.

Another approach to the solution of this problem was used in Ref.144. This is the only work so far which has taken into account the experimental fact that along the surface of contact of the components a wedge-shaped recess is formed in which the flame is located. The expression for the velocity of the flame in Ref.144 is found from the condition that at the 'tip' of the

*The velocity of propagation of a flame does not depend on pressure for only one system (KMnO_4 - perspex)¹²⁷ over a wide range of pressure (5-100 atm).

flame (i.e. at the point of the flame nearest to the unburnt mixture) the critical flow of substance is attained which can still be consumed by chemical reaction in a diffusion flame. The expression for the burning rate is obtained in an explicit form. Although this appears cumbersome, it is nevertheless clear that the rate of burning must depend on pressure. This is also in agreement with experiment.

An absolute value of the rate of burning is also given in Ref. 144. This evaluation agrees in order of magnitude with the experimental data of Ref. 124. Agreement with experiment would be better if the fact was included that the thermo-physical properties, especially the heat of vaporization, of the fuel and oxidizer usually differ greatly from one another. Therefore the actual recess in the layer of fuel is sharper than in the layer of oxidizer, whereas a symmetrical configuration was considered in Ref. 144. The evaluation¹⁴⁴ of the width d of the layer of component at which the burning rate ceases to depend on d , calculated to be $d_* \approx 0.026$ cm, can refer to the fuel but not to the oxidizer, which by experiment is $d_* \approx 1$ cm. In addition d_* depends on the pressure (see below).

E INCREASE OF BURNING RATE BY INTRODUCTION OF INERT ADDITIVES

It is useful to consider the fact that the mass (and even linear) burning rate of a condensed system can in principle be increased by the introduction of an inert additive¹³⁴.

According to (8) the mass burning rate is

$$m \propto \sqrt{\frac{2\lambda \phi_{\max}}{q} \cdot \frac{R T_c^2}{E}}$$

It follows that, other conditions being equal, m increases as the heat of combustion, q , decreases. This result is of little significance if q changes solely owing to the introduction of an inert additive.

The subscript 'a' (active) denotes quantities referring to the undiluted system, and the subscript 'in' (inert) denotes quantities referring to the inert additive. Quantities referring to the mixture (active substance + inert additive) are left without a subscript. The heat of combustion of a system with additive is $q = q_a (1 - \chi)$, where χ is the fraction of additive by weight. The rate of heat release in unit volume of flow is

$$\phi_{\max} = q_a (\text{cal/gm}_{\text{act}}) \cdot \dot{m}_{\max} (\text{gm}_{\text{act}} \text{ cm}^{-3} \text{ sec}^{-1}),$$

where \dot{W}_{\max} is the mass rate of reaction of active substance in a mixture containing inert additive (at $T = T_c$). Neglecting the change in λ and E , we obtain

$$\begin{aligned} \frac{m}{m_a} &\propto \frac{1}{1-\chi} \cdot \frac{T_{\max}}{(T_{\max})_a} \sqrt{\frac{\dot{W}_{\max}}{(\dot{W}_{\max})_a}} \\ &\propto \frac{1}{1-\chi} \left[\frac{T_{\max}}{(T_{\max})_a} \right]^{1-n/2} (1-v')^{n/2} e^{\frac{E}{2R} \left[\frac{1}{(T_{\max})_a} - \frac{1}{T_{\max}} \right]}. \quad (93) \end{aligned}$$

If only extremely small particles are considered, then v' , the fraction of the volume occupied by the particles in the two-phase flow, is exceedingly small (i.e. $1 - v' \approx 1$). In equation (93) as χ increases, the factor $1/(1-\chi)$ causes m/m_a to increase, whereas a very sharp reduction of $\dot{W}_{\max}/(\dot{W}_{\max})_a$ resulting from the reduction of $T_{\max}/(T_{\max})_a$, causes m/m_a to decrease. The resulting value of m/m_a for an inert additive can be either less or greater than unity, but not larger than $1/(1-\chi)$, thus the limiting value of m/m_a is 1.11 for $\chi = 0.1$ and 1.25 for $\chi = 0.2$, etc.

The significance of the factor $1/(1-\chi)$ in equation (93) becomes clear, if m is written as the sum of the flow of active substance $m(1-\chi)$ and inert additive $m\chi$. Then for the mass burning rate of active substance

$$(1-\chi)m \propto \sqrt{\frac{1}{q_a} \lambda \dot{W}_{\max} \frac{RT_{\max}^2}{E}}$$

i.e. the mass burning rate of active substance can only decrease with increase in χ .

Thus the term $1/(1-\chi)$ describes the increase of mass burning rate as a result of addition of a mass of inert substance. With the addition of inert particles of low specific heat and high density the limiting value $\frac{m}{m_a} \propto \frac{1}{1-\chi}$ can be approached quite closely. It is not very difficult to

obtain the expression for the linear burning rate by using expressions similar to those given in section 7,B

$$\frac{u}{u_a} = \frac{m}{m_a} \frac{\rho_a}{\rho} = \left(1 + \frac{\chi}{1-\chi} \frac{\rho_a}{\rho_{in}}\right) (1-v')^{n/2} \left[\frac{T_{max}}{(T_{max})_a}\right]^{1-n/2} \frac{E}{2R} \left[\frac{1}{(T_{max})_a} - \frac{1}{T_{max}}\right].$$

... (94)

In this expression the factor $\left(1 + \frac{\chi}{1-\chi} \cdot \frac{\rho_a}{\rho_{in}}\right)$, which increases as χ increases, gives the upper limit of the increase of u/u_a . This is related to the fact that for the same rate of reaction in the gas phase the linear rate of burning of the system with inert additive must be higher so as to be able to supply the necessary amount of substance in the reaction zone (small inert particles occupy an appreciable part of the volume in the solid phase and a negligibly small one in the two-phase flow).

9 MULTIDIMENSIONAL CHARACTER OF BURNING OF CONDENSED MIXTURES

For extremely finely dispersed ($d < d_{min}$) mixtures with vaporizable components combustion takes place in the kinetic regime, and the combustion front is plane (Fig.18a). When d becomes greater than d_{min} the mixing cones cease to be enclosed within the boundaries of the preheating zone. At the surface of the combustion front cone shaped projections appear, where combustion already displays a diffusion character (Fig.18b). The size of the projections increase as d increases and the surface of the combustion front becomes more and more distorted (Fig.18c).

It should be noted however that for any value of d , however large, the 'tips' of the flame are located in a homogeneous mixture, since the mixing of the components starts earlier than the reaction between them. Correspondingly burning at the 'tips' of the flame (in a zone of width about d_{min}) takes place in the kinetic regime, but above this is located the diffusion flame (height about md^2/D).

The surface of the condensed phase, generally speaking, is not plane even for $d < d_{min}$ because of the difference in the rate of vaporization of the components. For large values of d deep recesses inside which burning takes place are formed along the surface of contact of the components.

Thus for $d > d_{min}$ combustion of condensed mixtures is essentially multi-dimensional. The combustion front consists of a series of tongues of flame.

the 'tips' of which penetrate deeply into the condensed phase along the surface of contact of the components. In their upper part the tongues of flame merge together into a single diffusion flame.

The multidimensional character of the surface of the condensed phase can be clearly observed by means of cine-photographs during combustion (Fig.19) and also by the examination of burnt charges. Under certain conditions the oxidizer crystals form the projections and the fuel the recesses; under other conditions the reverse may happen. Observation of the burning surface is frequently made more complicated by the fact that the vaporization of each given oxidizer crystal or of fuel is a non-stationary process. In addition there is frequently a liquid or solid condensed residue on the surface. When studying extinguished charges errors can result from the non-homogeneous extinguishing of the charge (the time during which the vaporization process can be suppressed may be different for the fuel and oxidizer).

Experimental observations^{105,146,147,217} have shown that at high pressures and high burning rates the crystals of NH_4ClO_4 form recesses on the surface, and the fuel projects. At low pressures and low burning rates this difference is smoothed out or the oxidizer crystals begin to project. Thiokol polymer was used as fuel in Ref.105, and 2.4 parts by weight unsaturated polyester and 1 part by weight nitroglycerine was used in Ref.146.

This type of structure of the surface of charges was observed²¹⁷ for mixtures of NH_4ClO_4 with malonic acid and succinic acid and starch. For a mixture of NH_4ClO_4 with naphthalene (a very volatile fuel) only NH_4ClO_4 was found on the surface of extinguished charges along with a small quantity of the decomposition products of naphthalene. On the other hand for a mixture of NH_4ClO_4 with tungsten there was an accumulation of tungsten (the non-volatile component) on the surface.

In section 6,C the results of investigations¹²⁴ were mentioned in which measurements were made on the shape of the recesses formed on a plate of perspex during combustion in the following system: layer of KClO_4 of thickness d between two thick plates of perspex. The experiments were conducted in nitrogen at 1 atm abs and the flame was suddenly extinguished at a known time by a stream of water. The profile of the plate was measured under a microscope with micrometer traverses on three mutually perpendicular axes. In Fig.20 is shown the mean profile, taken over many measurements, of the recess for oxidizer layers of thickness 25 and 3.8 mm. The angle of burning ϕ (i.e. the angle between the tangent to the profile of the recess and the

direction of propagation of the flame) decreases smoothly in proportion to the distance from the flame 'tip'. In the initial portion (2 to 3 mm) the mean value of ϕ is $\sim 32^\circ$ for $d = 25$ mm and $\sim 13^\circ$ for $d = 3.8$ mm. The burning rate increased with decrease of d (from 0.50 mm/sec for $d = 25$ mm to 0.97 mm/sec for $d = 3.8$ mm). Thus the angle of burning becomes less as the burning rate increases owing to the decrease in d .

The angle of burning also becomes less if the burning rate increases owing to increase in pressure. In the same work¹²⁴ the mean angle of burning was measured for thickness $d = 0.9$ mm for vinyl plastic:

p, atm	10	20	30	40
u, mm/sec	1.37	2.12	2.43	2.73
ϕ_m	19°	$14^\circ 50'$	$14^\circ 40'$	13°

These results can be expressed by the empirical relationship $\sin \phi \approx 0.4 u^{-0.55}$.

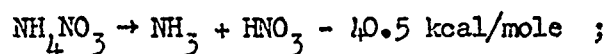
It was not possible to obtain¹²⁴ reliable measurements of the angle of burning in the oxidizer layer, since in extinguishing the charge with water the surface of the oxidizer layer was damaged. Measurements carried out during combustion, in the case of such oxidizers as KClO_4 , KClO_3 , KNO_3 and BaO_2 , are made more complicated by the presence of condensed residue. Approximate measurements (based on the appearance of temper colours on needles introduced into the oxidizer layer) gave $\phi \approx 55-65^\circ$ for KClO_4 at 1 atm abs and $d = 25$ mm.

10 MULTISTAGE BURNING OF CONDENSED MIXTURES

In the case of systems of mixtures with vaporizing components (for $d > d_{\min}$) there are two combustion zones: at points in the flame which are not very close to the unburnt mixture combustion take place in the kinetic regime and the diffusion flame is located above.

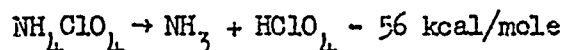
It is suggested^{97,104,118 et al.} that for systems based on NH_4NO_3 and NH_4ClO_4 a third zone also exists in which an exothermic reaction occurs. In this zone, located immediately above the surface of the oxidizer crystal, combustion of the vaporization products takes place.

In the case of NH_4NO_3 vaporization of the oxidizer proceeds according to the reaction:



ammonia and nitric acid vapour form a flame with a calculated temperature of $\sim 1250^\circ\text{K}$ ^{97,118} near to the surface of the crystal.

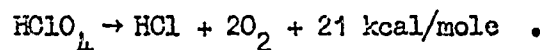
In the case of NH_4ClO_4 the oxidizer vaporizes by the reaction:



and the ammonia and perchloric acid vapour burn near the crystal surface with a calculated flame temperature of 1380°K at 1 atm abs¹⁵⁰.

It would be interesting to study the characteristics of the $\text{NH}_3 + \text{HClO}_4$ flame directly but this is not possible due to experimental difficulties. However successful studies have been made of the combustion of HClO_4 alone (decomposition flame) and the combustion of mixtures of HClO_4 with H_2 , CH_4 , CO and other fuels^{148,149}.

The decomposition of HClO_4 at high temperatures proceeds according to the reaction¹⁴⁸:



The combustion of the vapour was studied¹⁴⁸ of 72% aqueous HClO_4 solution which corresponds to $\text{HClO}_4 + 2.17 \text{ H}_2\text{O}^*$ at 210°C . The burning rate was $u_m \approx 19 \text{ cm/sec}$, $m \approx 0.021 \text{ gm cm}^{-2} \text{ sec}^{-1}$; the calculated flame temperature was 1076°K .

The rate and temperature of burning increase considerably with the addition of a gaseous fuel to the HClO_4 vapour (Table 33).

*Anhydrous HClO_4 is too unstable.

TABLE 33

Mass rate of burning and combustion temperature of homogeneous mixtures
 $(\text{HClO}_4 + 2.17 \text{H}_2\text{O} + x\text{N}_2) - \text{gaseous fuel}^{149}$, $p = 1 \text{ atm abs}$, $T_0 = 210^\circ\text{C}$

Fuel	x	m, gm/cm ⁻² sec ⁻¹				$\alpha_{u \text{ max}}$	$\alpha_{T \text{ max}}$	T_{max} , °K	$T_{\alpha=1}$, °K
		$\alpha = 1$	$\alpha = 0.667$	$\alpha = 0.5$	$\alpha = 0.4$				
CH ₄	1	0.48	0.558	0.46	0.41	0.67	0.90	2630	2620
CO	0	0.285	0.334	0.388	0.37	0.50	-	-	-
CH ₃ OH	2	0.459	0.503	0.395	-	0.72	0.91	2520	2505
C ₂ H ₆	1	0.502	0.545	0.482	-	0.72	0.84	2650	2640

For the same flame temperature, the burning rate of mixtures with HClO_4 is higher than for those with oxygen¹⁴⁹. Hence HClO_4 does not simply decompose to release oxygen, but is also a more active oxidizer. The mass burning rate of pure NH_4ClO_4 at 1 atm abs and $200\text{--}220^\circ\text{C}$ ⁴⁷ is 0.029 to $0.036 \text{ gm cm}^{-2} \text{ sec}^{-1}$, i.e. it is considerably less than the value of m for mixtures of HClO_4 with gaseous fuels. This is not unreasonable since the vaporization of $\text{NH}_4\text{ClO}_4 \rightarrow \text{NH}_3 + \text{HClO}_4$ is a strongly endothermic process and the combustion temperature of NH_4ClO_4 is low (1380°K).

The mass burning rate of NH_4ClO_4 - polyester mixtures¹⁵¹ at 1 atm abs and 200°C lies within the limits 0.20 to $0.27 \text{ gm cm}^{-2} \text{ sec}^{-1}$, i.e. it is quite close to the value of m for mixtures of HClO_4 with gaseous fuels, although it is smaller.

Direct observations on the kinetic combustion zones under consideration are extremely difficult, since the distance from these zones to the surface of the charge can be calculated to be 10^{-3} to 10^{-5} cm . Only during the burning of relatively large (several millimeters) spheres of NH_4ClO_4 in propane²³² are two combustion zones clearly observed on cine-photographs, and that directly adjoining the surface of the sphere apparently results from the combustion of $\text{NH}_3 + \text{HClO}_4$.

A LEADING STAGE OF COMBUSTION

In chapter I it was observed that combustion can proceed in several widely separated stages in homogeneous condensed systems and in even homogeneous gaseous systems. This is related to the special characteristics of

the chemical reaction kinetics in such flames since the reactions proceed stepwise. Such a 'multistage chemical' character can also be associated with systems of mixtures. However, the existence of several combustion zones, considered at the beginning of section 10, is associated not with the 'multistage chemical' character but with the presence in the system of two different components (one of which - the oxidizer - is capable of self-sustained burning) and with the multidimensional character of burning.

The problem of multistage burning is the question of the extent to which each stage influences the burning rate, or in other words to what extent the burning rate changes, if the reaction in a given stage is either retarded or accelerated, without changing the rate of the reaction in the other stages.

In section 5 this question was examined for homogeneous systems. For homogeneous systems the suggestion has been put forward in several papers (for example 138, 153 and others) that in multistage burning there is not infrequently one leading stage, which determines the burning rate. The remaining subsidiary stages are controlled by the burning rate.

This supposition seems reasonable for a plane combustion front which was considered in the works mentioned above. In fact there is a single value for the burning rate for a plane combustion front with a given temperature and composition of reagents¹⁵⁴. If a catalytic additive is introduced, which, for example, increases the rate of decomposition of the initial substance into intermediate products, without changing their temperature or composition, then the leading reaction zone begins to be moved by the increased flow of intermediate products in a direction away from the surface of the charge, until, as result of the decrease in heat flow from the leading stage, the velocity of the subsidiary stage again returns to its original value. At the same time only the temperature profile changes throughout the whole combustion zone, and in particular the temperature decreases at the surface of the charge.

This treatment refers to the case where the leading stage is located further from the unburnt mixture than the subsidiary stages. Alternatively, when the subsidiary stages are located further away than the leading stage, then if there is an increase in the rate of the leading stage and an unchanged rate of reaction in the subsidiary stage, it would seem that the zone of the subsidiary reaction should be displaced by the flow, i.e. such a configuration would be unstable. In practice this does not occur (see section 5).

The existence of a leading stage during the burning of condensed mixtures was examined in Ref. 155.

When the multidimensional burning characteristics of condensed mixtures* for $d > d_{\min}$ (see above) are considered, the logical expressions which showed the necessity for a leading stage of combustion lose their significance.

In fact for multidimensional burning there is no single value of the rate for a given temperature and reagent composition, since there is an additional independent parameter - the area of the combustion front for unit cross-section of flow.

As an example consider the fairly common case of condensed mixtures in which the oxidizer is capable of self-sustained combustion and the fuel is able to vaporize as a result of heat transfer from outside. The intermediate products formed during the burning of the oxidizer mix with the intermediate products formed during the vaporization of the fuel and form a flame which near its 'tip' has a kinetic and above it a diffusion character.

Introduction of a catalytic additive, which for example accelerates the burning of the oxidizer but does not change either the temperature or the concentration of intermediate products, should rapidly change the form of the surface of the charge and the shape of the diffusion flame. Assume that initially the vaporization of the fuel and the oxidizer take place in the same plane. After addition of the catalyst, which accelerates the oxidizer decomposition, but does not have any effect on the vaporization of the fuel, the oxidizer particles will form recesses and the fuel will project. Consequently the shape of the diffusion flame changes. The burning rate also changes, since it could not remain constant for two different configurations of the combustion zone.

The diffusion flame is also not a subsidiary stage. Direct experiments (see section 13) show that on changing the velocity of a diffusion flame by changing the degree of mixing of the components the burning rate as a whole is changed.

Thus theoretical considerations show that the rate of multidimensional multistage burning is not determined by processes taking place in any one stage.

However the effect of the various zones on the rate of burning is not the same. For condensed mixtures the proposition remains valid that only those zones which are not too far away have any significant effect on burning.

*Multidimensional burning can also exist in homogeneous systems if it is accompanied by the formation of a condensed residue such as flakes of soot.

In section 10,B this is examined in more detail. However, it is necessary to bear in mind that the effect of the i -th stage on the rate of burning cannot be correctly assessed, if only the direct heat transfer from this zone to the unburnt substance is considered. The supplementary flow of heat from all the $(i-1)$ stages between the unburnt substance and the i -th stage, associated with the rise in temperature within the boundaries of these zones owing to the transmission of heat from the i -th stage, can be much more significant. Hence only that zone which is located far away not only from the unburnt mixture but also from the intermediate combustion zones is 'sufficiently far away'.

Direct observations of all the combustion zones of the systems of mixtures considered above present great experimental difficulties and have not yet been carried out. So far there has been even less success in using direct experiments to determine to what extent each of these zones affects the burning rate. Only indirect treatments of this problem exist in the literature.

It is suggested^{97,113,118} that for mixtures based on NH_4NO_3 the basic role is played by the $\text{NH}_3 + \text{HNO}_3$ flame near to the surface of the oxidizer crystals. The following arguments support this view:

(1) Many powders and model mixtures based on NH_4NO_3 have the same rate of burning as NH_4NO_3 without fuel, when NH_4NO_3 as well as the mixtures based on it contain the same catalyst.

(2) A change of the molecular weight of a polymer has a great effect on the rate of pyrolysis and hence must have a great effect on the characteristics of the diffusion flame*. However, the burning rate is practically independent of a change in the molecular weight of the polymer.

For mixtures based on NH_4ClO_4 it is proposed in Refs. 104, 141 and elsewhere that the basic role is played by the flame of the decomposition products of the oxidizer ($\text{NH}_3 + \text{HClO}_4$). It has been shown¹⁴¹ that it is necessary fundamentally to include the increase in temperature in the $\text{NH}_3 + \text{HClO}_4$ flame zone due to the transfer of heat from the diffusion flame which thus results in an increase in the burning rate.

An assessment of the distance Δ between the surface of a crystal of NH_4ClO_4 and the $\text{NH}_3 + \text{HClO}_4$ flame is given in Ref. 104. This distance was very small, of the order of a micron.

*This conclusion is far from obvious and moreover has not been verified experimentally.

Such an assessment is easily deduced from the heat balance equation on the assumption that the burning rate is determined only by the $\text{NH}_3 + \text{HClO}_4$ flame zone:

$$\rho u [c(T_s - T_o) + Q] = \lambda \left. \frac{dT}{dx} \right|_s \approx \lambda \frac{T_c - T_s}{\Delta} \quad (95)$$

where for NH_4ClO_4 $\rho = 1.95 \text{ gm/cm}^3$, $c = 0.26 \text{ cal gm}^{-1} \text{ deg}^{-1}$, the heat of vaporization $Q = 56 \text{ kcal/mole} = 477 \text{ cal/gm}$ and also $\lambda \approx 2 \cdot 10^{-4} \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$, $T_c = 1110^\circ\text{C}$.

At 35 atm ($T_s \approx 680^\circ\text{C}^{130}$, $u \approx 0.3 \text{ cm/sec}$) a value $\Delta \approx 2.3 \mu$ is obtained from (95) and at 70 atm ($T_s \approx 720^\circ\text{C}^{130}$ and $u \approx 0.7 \text{ cm/sec}$) a value $\Delta \approx 0.9 \mu$.

Although the experimental dependences of the burning rate of multistage combustion on the pressure and initial temperature, etc, differ very little from the parallel relationships for single-stage burning, theoretical expressions have not yet been obtained for the burning rate of multistage combustion (see section 5). It is true that Summerfield's equation¹⁰⁵ for the dependence of the burning rate of two-stage combustion (kinetic zone + diffusion zone) on pressure is widely used in the literature, i.e.

$$\frac{1}{u} = \frac{a}{p} + \frac{b}{p^{1/3}} \quad (96)$$

where a is determined by kinetic factors (in particular $a \propto e^{E/2RT_c}$). The coefficient b is determined by diffusion factors (in particular, $b \propto d$). However in the derivation of (96) a series of arbitrary assumptions* has been made and hence this should be regarded only as an empirical equation

*It is assumed that the vaporization products of the fuel and oxidizer form separate 'pockets' and also that the mass of a 'pocket' does not depend on the pressure and is small in comparison with the mass of an oxidizer crystal or layer of fuel. It is assumed also that the temperature gradient can be written in the form $(T_c - T_s)/(l_k + l_d)$, where l_k and l_d are the widths of the kinetic and diffusion zones, etc.

suitable for those mixtures in which the exponent ν in the equation $u = bp^\nu$ is greater than $\frac{1}{3}$.

B ZONE WHICH CONTROLS BURNING RATE

The proposition (formulated in Refs. 124, 156 and elsewhere) that the burning rate of systems of mixtures is not controlled by the whole of the reaction zone in which the initial mixture is converted into the final combustion products, but only by a certain part of it ('zone of influence', 'active combustion zone', etc) abutting on the charge surface, has proved to be most useful in explaining experimental data.

Some idea of the width of the zone of influence can be obtained from the experiments¹²⁴ on the propagation of a flame along the surface of contact of plane layers of perspex and $KClO_4$. Various thin films were pressed or deposited from solution on to the surface of the perspex layer. For polyethylene films of increasing thickness Δ , the velocity of the flame at first increased and then (Fig. 21) for a certain thickness Δ_* developed a plateau. The value Δ_* is evidently equal to the thickness of the film which can burn completely in the zone of influence. Further increase in thickness (above Δ_*) of the polyethylene film no longer has any effect on the burning rate, since the latter is unaffected by what occurs outside the zone of influence - whether polyethylene or perspex is burning there. With increase of pressure the value of Δ_* decreases (from $\Delta_* \approx 0.9$ mm at 10 atm gauge to $\Delta_* \approx 0.2$ mm at 30 atm gauge). If the angle of burning of polyethylene is equal to ϕ , then the height of the zone of influence is equal to $h_{infl} \approx \Delta_* \cot \phi$. For polyethylene the angle of burning was not measured. If it is assumed that the value of ϕ for polyethylene is the same as for vinyl plastic, then at 10 atm $h_{infl} \approx 0.9 \cot 19^\circ \approx 2.6$ mm, and at 30 atm $h_{infl} \approx 0.2 \cot 14^\circ \cdot 40' \approx 0.76$ mm.

The size of the zone of influence for ordered systems can also be evaluated from the dependence of the flame velocity u on the thickness of the oxidizer layer d_{ox} . With increase in d_{ox} the velocity of the flame at first falls and then at a certain value $(d_{ox})_*$ straightens out into a plateau (Fig. 54). As in the case of Δ_* the value of $(d_{ox})_*$ is equal to the thickness of layer which can burn completely in the zone of influence. The value $(d_{ox})_*$ is 5-6 mm for the $KClO_4$ -perspex system^{124, 127}. It is not possible to calculate the height of the zone of influence starting from $(d_{ox})_*$, since the angle of burning in the layer of oxidizer was not measured.

In the usual disordered mixtures the size of the zone of influence and the fraction of the components which succeeds in reacting in the zone of influence must depend on the particle size of the components and also on the pressure, etc. Special experiments in which the width of the zone of influence could be measured have not yet been carried out.

Nevertheless, some conclusions may be deduced from the experimental dependence of the burning rate on the degree of mixing of the components, the ratio of the components, the pressure, etc (see chapter III). For ordinary disordered mixtures the size of the zone of influence is evidently considerably less than for the ordered systems which have just been considered. For an oxidizer particle size of several hundred microns and not too low pressures it is not possible for the components to react completely in the zone of influence. The fraction of the components reacting in the zone of influence falls rapidly with increase of d , but the absolute size of the zone of influence evidently increases somewhat with increase in d .

The heat used to heat the particles which react a long way downstream from the zone of influence is not compensated, generally speaking, by the heat transferred from distant parts of the flame. The presence of such particles in the zone of influence results only in a loss of heat. In other words combustion in the zone of influence takes place in the presence not only of sources of heat (as a result of chemical reaction), but of heat sinks (heat exchange to particles reacting outside the zone of influence). Other conditions being equal, heat losses become higher as the temperature transfer coefficient of the particles increases, and the size of the particles decreases.

In many cases the components first vaporize and then subsequently react with one another. If the particle size of the components is sufficiently small, and their volatility high, the particles vaporize completely and the mixture ratio remains the same as in the initial mixture. However with increase in particle size of the components different fractions of fuel and oxidizer succeed in turning into gas within the boundaries of the zone of influence. Consequently the mixture ratio in the gas phase begins to differ

from the initial mixture ratio in the direction of an excess of the more volatile component*.

In section 6.0 it was noted that in the burning of ordinary disordered mixtures the rate of vaporization of the components depends on the heat of vaporization. Consequently mixtures that are not too finely divided contain more oxidizer in the gas phase within the boundary of the zone of influence than the original mixture, since the heat of vaporization of KClO_4 is close to zero and the decomposition of NH_4ClO_4 and NH_4NO_3 is accompanied by the formation of the $\text{NH}_3 + \text{HClO}_4$ (or $\text{NH}_3 + \text{HNO}_3$) flame and thus takes place with heat release. However, the vaporization of ordinary organic fuels requires a considerable expenditure of heat.

C MODEL: COMBUSTION OF AN OXIDIZER PARTICLE + VAPORIZATION OF A LAYER OF FUEL

Various works^{104, 141} et al. have already been mentioned in which it is suggested that the rate of burning of compositions based on NH_4ClO_4 is the same as the rate of burning of crystals of pure NH_4ClO_4 after making allowance for the temperature increase in the $\text{NH}_3 + \text{HClO}_4$ flame as a result of heat transfer from the diffusion flame.

However it is also necessary to take into account the rate of transfer of burning from one crystal of oxidizer to another through the fuel layer. It is therefore relevant to consider the following elementary model of combustion. Let the oxidizer crystals, identical in size, be distributed uniformly in the fuel. The time of burning of a portion of the charge of length $d_{\text{ox}} + d_f$ is equal to $(d_{\text{ox}}/u_{\text{ox}}) + (d_f/w)$, where u_{ox} is the rate of burning of an oxidizer crystal with allowance for the heat transfer from the flame, and w is the rate of vaporization of fuel as a result of the heat transfer from the diffusion flame. The mean rate of burning of the composition is

*In this respect the burning of not too finely divided condensed mixtures has some similarity to the diffusive burning of multi-component liquid fuels (for example petroleum oils) (see Ref. 49) or with the burning of liquid explosive mixtures²¹⁸. In these cases the composition of the vapour phase, in which burning takes place, also may differ considerably from the composition of the initial mixture in the direction of excess of the volatile component. However for liquid mixtures burning does not proceed steadily; the most volatile components burn first. Consequently the rate of burning can change continuously (for liquid explosive mixtures periodic oscillations were also observed in the rate of burning²¹⁸). On the other hand for condensed mixtures burning can proceed quite steadily; the fraction of the components which has not vaporized within the boundary of the zone of influence does not mix with the initial mixture, but is carried away to the zone of the diffusion flame, where its combustion is completed.

$$u = \frac{d_{ox} + d_f}{d_{ox}/u_{ox} + d_f/w} \quad (97)$$

The rate of burning u_{ox} and rate of vaporization w vary with pressure in different ways. For NH_4ClO_4 at $p < 100-125$ atm, $u_{ox} \approx bp$. On the other hand w , as can be seen in section 6,C, depends only slightly on pressure: $w \approx b' p^{0 \text{ to } 0.25}$. Taking as a first approximation $w = f(p) = b'$ and putting $d_{ox}/d_f = k$ in (97)

$$u = \frac{k + 1}{k/bp + 1/b'} = \frac{(k + 1)bb'p}{b'k + bp} \quad (98)$$

where b , b' and k do not depend on pressure.

It follows from (98) that, at pressures which are not too high, u depends considerably on pressure (at $bp \ll b'k$, $u \propto p$). On the other hand at sufficiently high pressures the rate of burning in practice flattens into a plateau* (at $bp \gg b'k$, $u = \text{const} = b'(k + 1)$). The explanation of this plateau is obvious: at high pressures the time of burning of an oxidizer crystal is negligibly small in comparison with the time of transfer of burning through the layer of fuel, i.e. the rate of burning of the charge is equal to the rate of vaporization of the layer of fuel multiplied by $(k + 1)$.

Although this model is very primitive, it can evidently express the characteristics of burning of systems with binder of very low volatility.

11 EFFECT OF CONDENSED RESIDUE ON THE DEPENDENCE OF BURNING RATE ON PRESSURE

In some cases vaporization of the fuel or oxidizer is accompanied by the formation of a solid or liquid residue.

In certain cases, for example for mixtures based on $KClO_4$, a layer of residue of a definite finite thickness is formed on the surface of the charge; for the stationary regime of burning the rate of formation of condensed residue

*Taking the value $w \approx 0.5$ mm/sec for the rate of vaporization (see section 6,C) and the value ~ 5 , corresponding to $\sim 30\%$ of binder by weight, for the quantity $k = d_{ox}/d_f$, the limiting burning rate is $u_{\max} \approx 3$ mm/sec, which is reasonable.

on the surface of the unburnt substance is equal to the rate at which the condensed residue is removed by the gas at the external surface of the layer. Burning of the vaporization products can take place either under the layer of residue or inside it (in bubbles or streams).

In other cases, for example during the burning of KNO_3 or BaO_2 in coatings of perspex, the layer of condensed residue increases continuously as burning proceeds. The volume of slag formed can be roughly equal to the volume of the original charge, or even exceed it. Burning of the vaporization products takes place inside the layer of residue.

Obviously the presence of the layer of condensed residue can have a marked effect on the mixing of the components, on the heat transfer from the combustion zone to the unburnt substance, etc, and thus also on the dependence of the rate of burning on the various parameters. As yet this problem has been investigated only to a very small extent.

Only one possible mechanism for the influence of the condensed residue on the relationship $u(p)$ is considered in this section.

Usually the rate of burning of condensed systems (both heterogeneous and homogeneous) increases monotonically with increase of pressure so that the exponent ν in the equation $u = bp^\nu$ remains greater than zero.

However a fair number of systems has been described for which $\nu = 0$ over a definite range of pressures. Much more rarely are found systems for which $\nu < 0$ over a certain pressure range. Burning, for at least some of these systems, is accompanied by the formation of a condensed residue, for example the burning of a mixture $3\text{Mg} + \text{Cr}_2\text{O}_3$ ¹⁵⁷, burning of potassium picrate⁷⁰, burning of BaO_2 in a coating of perspex¹²⁷, etc.

It was shown¹⁵⁸ that under defined conditions the presence of condensed residue alone can lead to $\nu < 0$.

Let the system react in two stages and neglect their interaction, on the assumption that it is insignificant; the second stage is taken to be the leading one which completely determines the velocity of the first stage. In the first stage the original mixture decomposes with the formation of condensed residue (χ gm for 1 gm of original mixture) and gaseous intermediate products $((1 - \chi)$ gm for 1 gm of original mixture). The latter react in the second stage.

The condensed residue forms a dense layer of thickness y_u , through which bubbles or streams of gaseous intermediate products burst, but for

$y > y_*$ this layer breaks up. Consequently increase of y through $y = y_*$ causes the velocity of the gas to fall.

At a certain pressure the zone of the leading reaction is considered to be outside the dense layer. With increase in pressure this zone will come close to the unburnt substance. However as soon as it comes close to the dense layer (at $p = p'$), an increase in the rate of the reaction in the gas phase cannot increase the burning rate, since the reaction zone cannot penetrate into the layer of condensed residue, where the gas velocity is higher than the burning rate. From this point and so long as the pressure is insufficient for the penetration of burning into the layer of condensed residue, the relationship $u(p)$ will be determined by the relationship $y_*(p)$.

Another possibility is that increase of pressure should increase the thickness of the dense layer of residue y_* . Consider for instance the case where there is a layer of viscous liquid or of a conglomeration of particles and where the residue is carried away due to bursting of the viscous film by the emergence of a bubble of gas on the surface. In such a regime the rate at which the residue is carried away is proportional to the flow of the bubbles Π and to the square of the radius of the bubbles. For the thickness of the layer of residue to be stable, it should not be too large and should be such that in the length y_* a considerable expansion of a bubble could take place. If this condition is fulfilled, then for a chance decrease in y_* , the radius of the bubbles emerging on to the surface of the layer decreases, and thus the rate at which the residue is carried away becomes less than its rate of formation, so that y_* increases to a stationary value, although this is possible only for a definite value of χ .

The change in y_* with change in p is now considered. Let for $p < p'$, where p' is the pressure at which the reaction zone 'settles' on the dense layer of residue, the burning rate be proportional to p^ν , where $\nu > 0$. The volume flow of gas across the layer of residue is proportional to $p^{\nu-1}$, hence, for $\nu < 1$, Π should decrease or the volume of the bubble in this cross-section should decrease as the pressure increases, but y_* depends on the rate of expansion of the bubble inside the layer. As long as $p < p'$, the increase in y_* has no effect either on the burning rate or on the dependence of the burning rate on pressure, if the change in thermal conductivity is neglected. However, for $p > p'$ an increase in y_* should lead to a reduction in the burning rate. For a further increase in pressure burning is either extinguished or penetrates inside the layer of residue, i.e. there is a transition from one combustion regime to another.

As well as when y_* increases with increase of pressure, a maximum can be observed on the curve $u(p)$ for those cases where at low pressures a dense condensed residue is generally not formed, but at a certain pressure p_* a residue is deposited and forms a dense layer. Consequently at $p = p_*$ the burning rate can begin to fall with increase in p .

It would be of interest to follow the change of density and width of a layer of condensed residue with change in p for those systems for which $v < 0$ over a certain pressure range. This is difficult since the width of the zone influencing the burning velocity cannot exceed tens of microns. The concepts considered indicate that systems with $v < 0$ should be sensitive to effects influencing the thickness and density of the condensed residue.

Thus the form of the curve $u(p)$ could be changed, for example, by addition of substances preventing the formation of a conglomerate layer, or of volatile additives which break up the layer, or by directing a sufficiently powerful stream of gas on to the surface.

CHAPTER III

DEPENDENCE OF BURNING RATE OF CONDENSED MIXTURES ON VARIOUS PARAMETERS (EXPERIMENTAL DATA)

There are more parameters influencing the burning rate for condensed mixtures than there are for other types of systems:

	Condensed mixtures	Homogeneous gaseous mixtures	Homogeneous condensed explosives
Nature of components	+	+	+
Oxidizer/fuel ratio	+	+	-
Pressure	+	+	+
Initial temperature	+	+	+
Particle size of components	+	-	-
Relative density	+	-	+
Catalytic additives	+	+	+

It should be emphasized that each of the parameters listed affects the burning rate of condensed mixtures not in isolation but in close association with the others. Thus, for example, the shape of the curve $u(p)$ can depend to a great extent on α , and in some cases also on d and T_0 . In turn, pressure can influence the curve $u(\alpha)$, etc. The most important cases of these interdependences will be examined in the following sections.

Several investigations on the burning of systems of mixtures refer to solid propellents and compositions which are models of them based on NH_4ClO_4 . Consequently data on the burning of pure NH_4ClO_4 (see section 19) and NH_4NO_3 are of special interest. The mechanisms of flame propagation in ordered systems composed of plane or cylindrical layers of components (see section 18) are also examined. A short section is devoted to the burning of black powder, the oldest system of mixtures (section 20).

Where possible the experimental results will be considered in association with the views on the burning of condensed systems proposed in Chapter II.

*The shape of the particles (and in some cases the orientation of the particles with respect to the burning front) is also important.

12 TYPES OF CONDENSED SYSTEMS: METHODS OF MEASURING BURNING RATE

Condensed systems are outstanding in the great diversity of their use, the characteristics of their components, their composition, etc. Hence the absolute magnitude of the burning rate and the dependence of the burning rate on the various parameters can change considerably in the transition from one group to another.

Condensed systems can be divided according to their use into solid propellant mixtures (for rocket motors and various types of jet engines, for further details see the books of A.A. Shidlovskii¹⁵⁹, Ya. M. Paushkin²²², B.V. Orlov and G. Yu. Mazing²²³, etc) and pyrotechnic mixtures (igniter, flare and incendiary compositions¹⁵⁹, etc).

The nature of the fuel in a given composition is of great importance for the theory of burning which is discussed in the present work. The compositions can be divided into the following groups:

(1) Compositions which use an organic fuel that vaporizes at a moderate temperature and use a metal only as an additive to increase the specific impulse.

(2) Compositions which use a metal (usually magnesium or aluminium) as the basic fuel and use an organic fuel only as an additive to improve the mechanical properties of the charge.

The combustion mechanisms of these two groups differ markedly. As the proportion of fuel to oxidizer is changed the maximum burning rate u_{\max} for the first group is found close to the stoichiometric composition; generally, for a small excess of fuel, $\alpha = 0.7$ to 0.9 , whereas for the second group of mixtures u_{\max} is often considerably displaced in the direction of excess fuel (down to $\alpha \leq 0.1$).

The dependence of the burning rate on the particle size of the components for the first group is less than for the second. On the other hand a slight dependence of the burning rate on pressure is much more frequently observed for mixtures belonging to the second group.

In the present work the first group is mainly examined, since the majority of the literature data refers to such mixtures.

Methods of measuring burning rate

Existing methods of measuring the burning rates of condensed systems can be divided into three groups depending on the physical phenomenon associated

with combustion which is utilized in the particular method (Table 34). Under laboratory conditions, methods involving the fusing of fine wires are the most frequently employed and the break in the circuit is determined by means of a loop oscillograph, etc. Ordinary or high-speed cinematography is often used. Alternatively, the duration of burning is determined from the $p(t)$ curve using a low-inertia pressure transducer. Photorecording has been used in numerous experiments. Occasionally, as in Ref.161, where the temperature profile is measured by thermocouples, it is possible to determine the burning rate from the records of two thermocouples located at a known distance from each other.

Generally, only the mean burning rate \bar{u} is measured in a rocket motor; the time τ elapsing between the beginning and end of burning is determined from the $p(t)$ curve, whence $\bar{u} = l/\tau$ where l is the thickness of the web of the charge. In all cases when the burning rate is to be determined at different points of a charge, the charge is extinguished at a definite time after the beginning of burning and the extinguished charge is then measured at various sections (see, e.g. Ref.236). Occasionally, a burning charge is photographed through a window or through the wall of a transparent chamber made of perspex.

The choice of a particular method of measuring burning rate depends on the experimental conditions, such as laboratory apparatus or rocket motors, experiments in vacuo, at atmospheric pressure or at high pressures, etc. It is also important whether it is required to measure only the mean burning rate, or the burning rates at different points of the charge, or to confirm that the rate is constant in time. In some cases the properties of the mixture can be a deciding factor; for example, the burning rates of mixtures with very transparent or very dim flames are unsuitable for measurement by photographic methods. It is also necessary to consider the accuracy of a particular method. Finally, the choice of a method may be influenced by the possibility of obtaining additional information besides the measurement of burning rate; thus, for example, cinematography allows study of the form of the surface of the charge, the flame shape and luminosity, etc.

The methods of measuring the burning rate in laboratory conditions are now considered in further detail.

Methods of

Phenomenon on which method is based	Methods of measurement	Quantity measured	Continuity* and accuracy** of measurement
Luminosity of the flame or the difference in the absorption coefficient of the unburnt and reacted substance	Photorecorder	Linear rate ascertained along a certain line on the surface of the charge	Direct continuous measurement
	Cine-camera	Linear rate and shape of front in one lateral projection	Direct measurement; continuity determined; ratio of burning to camera speed
	Photoelements, photo-resistance	Linear rate along surface of charge	Either direct or indirect continuous measurement
Increase of temperature and extent of ionization in the combustion front	Fine wires that burn through	Linear rate between small number of points at a depth below or on the surface of the charge	Direct discrete measurement
	Ionization detectors	Linear rate between small number of points at a depth below or on the surface of the charge	Direct discrete measurement
	Thermocouple, thermoresistance	Linear rate between small number of points at a depth below or on the surface of the charge	Direct discrete measurement
Increase of pressure	Pressure transducer of low inertia	Mass rate	Indirect continuous measurement
		Linear rate between a small number of points	Direct discrete measurement

*In a continuous measurement the rate of burning is determined at a particular point of a charge.

**In the case of a direct measurement, the progress of the combustion front is (for example, the development of pressure in an enclosed space).

A

TABLE 34

Methods of measuring burning rate

Accuracy* and directness** of measurement	Reaction of detectors on process being measured	Laboriousness of experiments and calculations	Remarks
Continuous measurement	Absent or (for short exposure) very small	Experiments and evaluation of results are simple	Transparent coating on the charge and windows in apparatus are necessary, also careful orientation of charge
Measurement; continuity determined by rate of burning rate camera speed	Absent or (for short exposure) very small	Experiments are simple; evaluation of film is tedious	Transparent coating and windows in apparatus are necessary. Usually the film consumption is high
Direct discrete direct continuous measurement	Absent or (for short exposure) very small	Experiments are simple; evaluation is simple for discrete measurements	
Discrete measurement	Increases with increase of number of detectors, increase of size of detector, and reduction of distance between detectors	Time consumption in mounting. Difficulty of instrumenting the charge increases with increase in number of detectors; evaluation very simple	
Discrete measurement	Increases with increase of number of detectors, increase of size of detector, and reduction of distance between detectors	Time consumption in mounting. Difficulty of instrumenting the charge increases with increase in number of detectors; evaluation very simple	
Discrete measurement	Increases with increase of number of detectors, increase of size of detector, and reduction of distance between detectors	Time consumption in mounting. Difficulty of instrumenting the charge increases with increase in number of detectors; evaluation very simple	
Not continuous measurement	Absent	-	
Discrete measurement	Absent when registering only the start and finish of burning. Can be significant on introduction of intermediate layers	When recording only the start and finish of burning, experiments and evaluation are very simple	When only the start and finish of burning is recorded the accuracy of measurement is low

particular point of a charge, and in a discrete measurement, the mean rate between individual

in front is measured, and in the case of an indirect measurement, the secondary phenomenon

B

Constant and variable pressure bombs

In the laboratory the burning rate is usually measured on small cylindrical cigarette burning charges of diameter 5 to 15 mm, height 10 to 100 mm, burning from the top downwards. Since the velocity of the flame along the free surface, i.e. boundary with the gas, of the charge can exceed the normal velocity, the lateral surface of the charge is coated with a layer of lacquer, resin, cement, etc, or an inert gas is blown on to it (upwards from below) or the charge is pressed into a casing of metal or perspex*.

At pressures above atmospheric experiments are carried out in air-tight vessels (bombs) capable of withstanding the necessary pressure. If the weight of the charge per unit volume of the bomb is sufficiently small so that the increase of pressure Δp as a result of combustion of the charge is small in relation to the initial pressure in the bomb p_0 , then the term 'constant pressure' bomb is used. In the case where Δp is comparable to p_0 or exceeds it, the term 'variable pressure' bomb is used. These terms are not strictly accurate, since in both cases the bomb is of constant volume; incidentally, this correct term is used in the study of burning of gas mixtures. However, these terms are widely used in the literature of the burning of condensed systems and are convenient to a certain extent. The constant pressure bomb is referred to as the 'Crawford bomb' or 'Crawford type bomb' in most foreign works.

There are various designs of constant pressure bomb, but they all consist of the same basic elements: the body, the lid (or, less often, two lids), piping for application of pressure to the bomb and for release of pressure, high voltage, $>> 100$ V, electric leads which supply the heating coil, electromagnets, ignition coils, etc, and low voltage leads from the thermocouple terminals; windows of perspex or glass⁶ for optical measurements;

*The casing should fit the charge very tightly, since otherwise there may be a sudden increase in burning rate as the flame is propagated with extremely high velocity along the gap³⁸.

⁶Perspex facilitates sealing of the window and possesses mechanical characteristics which are reasonably constant with respect to time, whereas glass needs very careful sealing and is also inclined to fracture owing to fatigue; cases have been observed where a glass window has broken under the application of a pressure several times less than that to which it had been subjected for a prolonged period. On the other hand, the optical characteristics of perspex are significantly worse than those of glass since, during sealing, the surface of perspex bulges to a marked extent; also perspex is easily scratched, scorched, etc.

leads for pressure transducers. In some cases there are also inlets for the thermostatic control liquids, various kinds of handles for mechanical movement of the charge or other component inside the bomb when the latter is under pressure, and so on.

The sealing of all these connections to the bomb is of great importance. This is effected by means of gaskets. Metal (copper or aluminium) or soft (rubber, teflon, fibre) gaskets may be used for parts which are only infrequently removed. . . Soft gaskets are preferable for the lids.

Constant pressure bombs usually work at $p \leq 150$ atm and the pressure is obtained by compressed nitrogen from standard cylinders. However, constant pressure bombs have also been designed for pressures of 500 atm³⁶, 1000 atm⁴² and higher pressures in which the pressure is obtained by a gas compressor.

The volume of a constant pressure bomb does not usually exceed 10 litres. A reservoir is used if necessary; a standard cylinder may be used as a reservoir at $p < 150$ atm. However, the higher the burning rate, the larger should be the free cross-sectional area of the pipes connecting the bomb with the reservoir, so that the pressure can be rapidly equalized.

As an example, the construction of the B 150 bomb designed by the Institute of Chemical Physics of the Academy of Sciences of the U.S.S.R. is shown in Fig.22. It is of 2 litre volume and has three perspex windows (20 x 40 mm), and four high voltage (several hundred volts) leads. There have been several modifications of B 150 bombs, for temperature measurements, etc.

Variable pressure bombs are the oldest devices for investigating the burning of powders at high pressures. The $p(t)$ curve is measured by means of simple mechanical transducers. The maximum pressure in the bomb may also be determined by the extent of compression of a small copper rod ('crusher'). From the shape of the $p(t)$ curve it is possible to obtain a tentative idea of the relationship $u(p)$ for the composition under investigation. Bombs of this type are often called manometric bombs and the maximum working pressure may reach several thousand atmospheres.

In modern variable pressure bombs low-inertia piezo-electric or strain gauge transducers are usually employed for recording the $p(t)$ curve. It is also possible in principle to utilize other methods for measuring the burning rate, such as the fusing of fine wires or even optical methods.

The use of a variable pressure bomb is exemplified in Ref.44 by a 4000 atm bomb to record $p(t)$ curves by means of piezo-electric transducers; charges consisting of several pellets with different burning rate were used - the start and finish of burning of each pellet was determined from the inflections in the $p(t)$ curve.

Some other laboratory methods of measuring burning rate are now considered in rather more detail than at the beginning of section 12.

Photographic recording

Photography of a flame on film continuously moving perpendicularly to the direction of propagation of the flame is one of the oldest methods of measuring the rate of burning or detonation. The apparatus is called a photorecorder ('fotoregistr' or 'fotoregistrator') in the Russian literature, but its principle of action is more clearly shown in the terms 'slit camera' or 'drum camera' used in the English literature.

There are two types of photographic recorder. In the revolving drum type the film is secured to the lateral surface of a revolving drum and the image of the charge is stationary (in the laboratory system of co-ordinates); in the other, using 'moving mirror' recording, the film is stationary and the image of the charge passes over the film by means of a rotating mirror (for more detail, see the book by A.S. Dubovik¹⁶⁰). Photorecorders of the first type can record rates not greater than 100-200 m/sec, whereas the other type can record rates up to several kilometres per second. In practice, revolving drum photorecorders are used for the study of combustion, and the rotating mirror type mainly for the study of detonation.

On the film from the drum camera the inclined line corresponds to the progress of the flame front; below the line the film is transparent, and above the line it is obscured by the combustion products (Fig.23). The burning rate is calculated from the equation

$$u = k v_{\text{film}} \tan \phi \quad (99)$$

where u is the burning rate, v_{film} the film speed, k the magnification factor of the camera and ϕ is the angle between the line recorded by the

flame front and the horizontal axis, which is the linear velocity vector of the film*.

The accuracy of the burning rate measurement is increased as the definition of the flame front on the film becomes sharper. It is not difficult to show that the most sharply defined front is obtained if the flame propagation is photographed through a certain sized narrow slit such that the luminous point or luminous edge moves perpendicularly to the direction of motion of the film.

There are two schemes for the optical system of a photorecorder. With a single objective the slit is located near the charge, whereas with the double-objective system the slit is located in the plane of the image of the charge formed by the first objective. The second objective reflects the slit and the intermediate image of the charge on to the film. In the first case the image of the front on the film is less sharp, since the charge and the slit are in different, though adjacent, planes, whereas in the second case the illumination intensity of the system is lower and focussing is more complicated.

Analysis of the errors in burning rate measurements using a drum camera shows¹⁶² that there is an optimum value of the angle ϕ at which the errors of measurement are minimised. For the combustion of small charges (of height 1 to 2 cm) for the single-objective camera $\phi_{\text{opt}} \approx 10-15^\circ$ and somewhat greater for the double-objective system.

The burning rate of condensed mixtures varies over a wide range (at least from 0.1 to 100 mm/sec) depending on the nature of the mixture, its composition, the pressure, etc. Consequently choice of film speed over a wide range is necessary so as to obtain photographs with ϕ not too far from ϕ_{opt} . Thus drum cameras for measuring burning rates are fitted with a reducing gear to give a wide range of operating speeds. Thus, for example, the drum photorecorder shown in Fig.25 designed by the Institute of Chemical Physics, Academy of Sciences, U.S.S.R. has a double-objective optical system and film speeds of 1, 2, 4, 8, 16, 32, 64, 128, 256, 512 and 1024 mm/sec.

*It is convenient to use a magnifying attachment for evaluating $\tan \phi$ on the film, as shown in Fig.24. The pivoted ruler is set parallel to the front of the image and the scale division marked on the edge of the attachment plate is read off; the value of $\tan \phi$ is calculated previously for each scale division.

It is not possible to reduce the slit width beyond the point where diffraction occurs. The practical slit width may be reached even earlier on account of the decreased light passing through the slit.

Measurements of \bar{u} by means of pressure transducers

This method determines the interval of time τ between the beginning and end of burning on an oscillogram showing the recorded curve of $p(t)$, both in constant pressure and variable pressure bombs. Then $\bar{u} = h/\tau$, where h is the height of the charge. The oscillogram also enables fluctuations of the burning rate to be detected. In constant pressure bombs it is convenient to use piezo-electric pressure transducers, since these can operate as differential pressure transducers; when supplying compressed nitrogen to the bomb, at a pressure measured by an ordinary manometer, the faces of the piezo-quartz crystal are earthed; the transducer is set in operation before the experiment is begun. The maximum amplitude of the beam on the oscillogram corresponds to Δp (the increase of pressure as a result of burning). The sensitivity of the piezo-electric transducer is easily controlled by varying the capacitance of the capacitor to which the electrical charge from the piezo-quartz crystal is fed, and also by altering the ratio of the area of the crystal to the area of the rod on which the pressure in the bomb acts.

A small weighed portion of rapid-burning composition (e.g. potassium picrate) may be fixed to the end of the charge so as to achieve vigorous ignition, and thus obtain a record of $p(t)$ which can be more easily interpreted. In this case 'steps' appear on the curve at the beginning and end of burning (Fig.26).

The above method is readily carried out, but is inferior as regards accuracy of measurement to other methods of determining \bar{u} in which the transducers are located at a sufficiently great distance from the ends of the charge.

Other methods of measuring the mean burning rate

As already stated, the most widespread laboratory method of measuring the (mean) burning rate is the strand burner method. A wire may be inserted through a hole drilled in the strand, but this is often unsatisfactory, since a brittle strand crumbles and the hole in an elastic strand becomes an incorrect shape; moreover it is difficult to pull a fine wire through the hole, etc. Alternatively, several pellets can be 'composited' or stuck together to form a charge, the wires being pressed between the pellets, in which case there is little difficulty in using fine wires and in measuring the vertical distance between them accurately. However there are possible errors connected with the change in burning rate at the moment of transition of burning from one pellet to the next.

The ionization detector used in Refs. 163-165 consisted of two wires to which was applied a voltage of 100-200 V; the gap between the wires was 1 mm. As the flame passed between the wires, the ionization gap was closed and a current was produced in the circuit which was measured by a loop oscillograph. Such ionization detectors were inserted between the first and second, second and third pellets, etc., of which the charge consisted. The time of burning is calculated in the same way as for the fusing of fine wires.

The propagation velocity of a flame along the surface of contact of cylindrical layers of metal powder with solid oxidizer was measured in Ref. 166 using instead of fine wires fine (0.3-0.6 mm) quartz fibres, which penetrated to the surface of contact through holes bored in the external layer. As the flame passed these fibres the light from the flame fell on a photocell and the signal was recorded by a loop oscillograph.

The methods of measuring \bar{u} by the fusing of wires, ionization detectors, photoelectric conductors, etc., are basically more or less equally accurate. From the experimental point of view, the first method (fusing of fine wires) is the simplest, although the second method is only slightly more complicated. The mounting of the detectors in the third method makes it more complicated than the two others. The choice of method is often dictated by the characteristics of the system to be measured.

13 DEPENDENCE OF BURNING RATE ON PARTICLE SIZE OF COMPONENTS

The dependence of the burning rate of condensed mixtures on the particle size of the components is of great practical interest, since it enables the burning rate to be controlled without changing the mixture composition and hence without changing the specific impulse of the propellant.

In preparing condensed mixtures it is necessary to consider the function $u(d)$, where d is the particle size of the components, so that the change in the burning rate from one batch of raw material to another, etc., does not exceed the permissible limits.

The dependence $u(d)$ is also of great theoretical interest, since it shows most clearly the effect of diffusion factors on the burning rate. The most significant part of the concepts of the burning of condensed mixtures is based on the study of this particular function.

A PARTICLE SIZE OF COMPONENTS

In general the burning rate of a condensed mixture depends both on the size of the oxidizer particles d_{ox} and on the size of the fuel particles d_f .

However if the fuel is plastic at the moment of mixing, it forms layers between the crystals of the oxidizer. The size of the layers of fuel is directly proportional to the size of the oxidizer particles ($d_f = (1/k) d_{ox}$). Hence for this case, which has the most practical significance, the dependence of u on the particle size of the components is similar to $u(d_{ox})$. A similar result will be obtained for a mixture of two components in powder form which readily vaporize, if the size of the particles of one component is much less than that of the other. A finely divided component forms layers, the size of which is proportional to the size of the particles of the coarse component. If, however, the finely divided component is non-volatile and does not conglomerate into an unbroken layer, the burning rate can depend on d_f as well as on d_{ox} .

So far it has been assumed that all the particles of a given component are the same size. In practice this condition may be only an approximation, valid when narrowly defined unimodal fractions are used.

Sieves of brass or bronze wire or of silk cloth are used to obtain fractions, for particle sizes greater than 30-40 μ . It is customary to regard fractions of type 40-50, 100-140, 300-400 μ as sufficiently unimodal. There is usually no advantage in using more narrowly defined fractions, since the accuracy with which the dependence $u(d)$ can be determined is not very high because of the differences in the particle size distributions for each fraction, the differences in the uniformity of mixing of the components, etc. In addition, the preparation of very narrow fractions is extremely time-consuming.

The original material used to prepare narrow sieved fractions should not contain any significant amount of fine particles ($< 10 \mu$), since these are very difficult to remove by sieving. If the original powder is too coarse for the required fraction, it should not be ground, since much fine powder is produced during grinding, but it should be recrystallized (naturally if this is possible) in such a way* as to obtain particle sizes close to those desired.

For a particle size less than 20-30 μ the preparation of narrow fractions by precipitation in a flow of liquid or gas or by other methods is a tedious

*If a saturated solution of $KClO_4$ or NH_4ClO_4 is cooled very quickly, for example, if the hot solution is poured in a thin film on to the surface of a massive metal vessel at a low temperature, then fine crystals are formed. On the other hand, very large (several millimeters and more) crystals are formed by the very slow cooling (tens of hours) of a saturated solution.

operation with low yields. Therefore for $d < 20-30 \mu$ polymodal fractions obtained by grinding in mills of various types are frequently used. Nevertheless such fractions are not infrequently characterized by some mean effective particle size which is usually calculated from the specific surface using the relationship

$$d_{\text{eff}} = 6/S_{\text{sp}} \rho$$

$$(\text{cm}) = 6/(\text{cm}^2/\text{gm})(\text{gm}/\text{cm}^3)$$

where ρ is the density of the particle.

In addition to the sieve size (which is usually defined as the arithmetic mean of the mesh size of the sieve used for obtaining the fraction, e.g. for the fraction* $-0.140 + 0.100$ the mean sieve size is 120), and to the effective size calculated from the value of the specific surface, the size obtained by microscope measurements is also used. In this method a sufficiently large number of particles (not less than a few hundred) is measured using a microscope with an ocular grid along two mutually perpendicular directions and then the arithmetic mean is taken, or other methods of obtaining the mean value can be used.

For the same fraction, the size by microscope measurements is usually larger than the mean sieve size, since elongated particles may shake through a sieve hole of a given size.

In contrast to systems with unimodal fractions, systems where the component under investigation is a mixture of two narrow fractions differing considerably in their particle size are of greater practical interest. Such systems can be used to study the dependence of the burning rate on the ratio of the coarse to the fine fraction, on the size of the coarse fraction (size of small fraction constant), and conversely on the size of the fine fraction (size of coarse fraction constant), etc. Naturally the dependence of the burning rate on the particle size is complex in this case and it is more difficult to form a clear picture of it.

In some investigations (e.g. Ref.167) the size of a fraction is characterized by a complete curve (usually an integral) of the particle size

*It is customary to denote by a minus sign (-) the mesh size of the sieve through which a given fraction passes completely and by a plus sign (+) the mesh size of the sieve which retains the given fraction.

distribution. This enables a better idea to be obtained of the particle size of the fraction, but so far it has not brought any perceptible advantage to the study of the dependence $u(d)$ and in fact for each fraction some mean size is calculated which is used in the dependence $u(d)$.

B EXTENT OF CHANGE IN BURNING RATE DUE TO CHANGE IN PARTICLE SIZE

It is of paramount interest to know the extent to which the burning rate can be changed by varying the particle size of the components. This question was specifically investigated in Ref.139.

$\theta_* = u_0/u_\infty$ is used to denote the ratio of the burning rate of the limiting case of a finely divided mixture $u_0 = u/d \rightarrow 0$ to the burning rate of the limiting case of a coarse mixture $u_\infty = u/d \rightarrow \infty$. Under actual conditions the range of change in particle size is not infinitely large. Even under laboratory conditions the most finely ground fraction of oxidizer usually has a particle size greater than 5 to 10 μ although metal powders can be considerably finer - down to 0.1 to 0.01 μ ; see for example Refs.171, 172. At the same time in practice it is impossible to mix components so carefully as to avoid agglomeration of the fine particles. The particle size in the coarsest mixtures does not exceed 300-500 μ and only in rare cases reaches 1-2 (in laboratory mixtures).

Thus in general the possibility of controlling the burning rate by changing the particle size can only be partially realised. The actual value of $\theta = u_{fi}/u_{co}$, where u_{fi} and u_{co} are the burning rates of the most finely and most coarsely divided mixture respectively remains less, often considerably less, than the limiting value $\theta_* = u_0/u_\infty$.

Experimental data show that for vaporizing components the dependence of burning rate u on particle size d is relatively slight and the extent of change of u due to change of d , as characterized by the quantity θ , is small. On the other hand for non-volatile components the dependence $u(d)$ is considerably greater and the quantity θ is considerably larger (Table 35). In other words by changing the particle size of a non-volatile component one can change the burning rate to a much greater extent than by changing the particle size of a component that easily vaporizes.

This phenomenon is evidently quite regular. From section 6,A, B it is seen that for systems with vaporizing components, the components can mix in the preheating zone at a reasonably high rate. Consequently the burning rate can be determined to a considerable extent by kinetic factors and the dependence $u(d)$ is slight, and for sufficiently small values of d it is completely absent, since mixing can be accomplished completely within the boundary of the preheating zone.

TABLE 35

Change in burning rate of condensed mixtures due to change in particle size of components

Mixture	α	Component for which $u(a)$ is investigated	Particle size of investigated component, μ		d_{co}/d_{fi}	$\theta = u_{fi}/u_{co}$				Ref.
			Finest, d_{fi}	Coarsest, d_{co}		5 atm	10 atm	40 atm	100 atm	
$KClO_4$ -bitumen	1	$KClO_4$	~10	1700	170	1.87	2.1	2.16	2.20	137
NH_4ClO_4 -polystyrene (ungelatinized mixture)	1	NH_4ClO_4	~6	230	~38	1.38	1.29	1.37	1.40	168
	0.5	NH_4ClO_4	~6	230	~38	1.21	1.38	1.56	1.54	
	0.2	NH_4ClO_4	~6	230	~38	-	-	1.11	1.42	
NH_4ClO_4 -polystyrene (gelatinized* mixture)	1	NH_4ClO_4	~6	230	~38	2.24	2.19	3.28	3.29	168
	0.5	NH_4ClO_4	~6	230	~38	1.68	2.33	2.56	3.04	
$KClO_4$ -graphite	0.4	Graphite	~2	125	~62	-	-	8.6	11.0	164
$KClO_4$ -W	~0.2	Tungsten	~2.7	550	~204	47.5	-	44.5 (50 atm)	31.7	139
	~0.1	Tungsten	~2.7	340	~126	40.7	41.2	33.4 (50 atm)	29.7	
Fe_2O_3 -Al	~1	Aluminium	0.1	550	5500	25.7	26.8	16.4 (50 atm)	17.2	139

*See section 14 for explanation.

On the other hand for systems where one component (usually the oxidizer) vaporizes and the other is non-volatile, mixing can occur only simultaneously with the reaction. In this case burning takes place in a regime close to the diffusion regime and there is a strong dependence $u(d)$ (where d is the particle size of the non-volatile component).

C SHAPE OF CURVE $u(d)$

In the previous section it was noted that when the particle size is changed the burning rate changes considerably in the case of the non-volatile component and slightly in the case of the vaporizing component. It is natural to expect that the shape of the curve $u(d)$ ought to be different for the two cases.

For the non-volatile component the shape of the curve $u(d)$ has been investigated only in Ref. 139. Experiments were carried out on $W-KClO_4$ mixtures with five different fractions of tungsten, four of which were obtained by sieving one batch of tungsten powder and the fifth from a powder with particle size $\sim 2.7 \mu$ belonging to a different batch. The particle size of the coarse fractions was characterized by a mean 'sieve' diameter and mean 'microscope' diameter; the particle size of the five fractions was also characterized by the effective diameter d_{eff} calculated from the specific surface area S_{sp} which was determined by drawing air through a layer of powder using apparatus PSKh-2:

'Sieve' fraction	+0.400	-0.400 - +0.140	-0.140 - +0.100	-0.040	Powder
d_{sieve}, μ	-	270	120	-	-
$d_{microscope}, \mu$	550	340	160	~ 13	-
d_{eff}, μ	-	-	-	~ 19	~ 2.7

The function $u(d)$ (or more precisely $\log u = f(\log d)$, Fig. 27) has a plateau for 'medium' values of d ¹³⁹. In other words for small values of d (~ 3 to 19μ) u is markedly dependent on d ($u \approx 1/d$); for 'medium' values of d (19 to 160μ) the dependence $u(d)$ becomes less strong and then at high values of d (160 to 550μ) $u(d)$ again approaches $u \approx \frac{1}{d}$. Because of lack of other experimental data it is not yet clear how real is the reduction of the dependence $u(d)$ for 'medium' values of d .

The shape of the curve $u(d)$ for particles of vaporizing components has been investigated in great detail (see Refs.137, 141, 146, 169, 170 and others).

It should be noted first that there is a 'normal' curve $u(d)$ for mixtures whose composition is not far from stoichiometric and an 'anomalous' curve $u(d)$ for mixtures with a very large excess of fuel, and possibly also for mixtures with a very small percentage of fuel, i.e. very large excess of oxidizer.

The 'normal' curve $u(d)$ is considered first. It was shown¹³⁷, using a stoichiometric KClO_4 -bitumen mixture, that at not too high pressures (for the given mixture up to 5 atm) the curve $u(d_{\text{ox}})$ has an S-shape (Fig.28): for the vaporizing component the burning rate is slightly dependent on the particle size for small values of d_{ox} ; then at 'medium' values of d_{ox} the burning rate falls considerably with increase of d_{ox} , but for large values of d_{ox} the dependence $u(d)$ becomes weaker. The first plateau, for sufficiently small values of d , evidently results from the fact that the mixing of the components is successfully completed in the preheating zone and burning takes place in the kinetic regime (see section 8,A).

With increase in pressure, and consequently in burning rate, the first plateau in the experimental $u(d)$ curves disappears. It is possible that it would still be observed at high pressures, if the experiments were carried out with even more finely divided mixtures, i.e. that the plateau is observed both at high and low pressures, but its length decreases as the pressure becomes higher.

The presence of a plateau for $d < d_{\text{min}}$ is confirmed by the results of experiments¹²³ which upheld that there is a definite value $u_{\text{min}} \sim 0.35$ to 0.45 mm/sec (the burning rate changed with increase in p for certain values of α), such that for $u < u_{\text{min}}$ the fine fraction (74 to 105 μ) and the coarse fraction (297 to 420 μ) of NH_4ClO_4 burnt in a stream of methane at the same rate.

The second plateau (for large values of d) results from the fact that an increase in d above certain limits no longer affects the processes taking place in the zone of influence. Among several investigations (including Ref.137) which showed a decreased dependence $u(d)$ for high values of d , the work of Ref.146 will be mentioned. For a composition (65% NH_4ClO_4 , 24% unsaturated polyester, 10% nitroglycerine, 1% additive) the experimental points were approximated by the equation $u \approx d^{-n}$ and the value of n was as follows:

d	n	
	p = 15 atm	p = 50 atm
less than 150 μ	0.57	0.59
larger than 150 μ	0.20	0.074

The curve $u(d)$ for a large excess of fuel is now considered. Experiments were carried out¹⁷⁰ with mixtures of NH_4ClO_4 * with polystyrene ($< 100 \mu$) for $\alpha = 0.15, 0.2$ and (for comparison) $\alpha = 1$, and also with perspex ($\sim 3 \mu$) for $\alpha = 0.2$ and (for comparison) $\alpha = 1$. It was shown that for mixtures with a large excess of fuel the burning rate increases with decrease in d only up to a certain limit, and then for a certain value of d goes through a maximum and begins to fall (Fig.29b, c, and Fig.30).

This paradoxical dependence $u(d)$ for mixtures with a large excess of fuel can be explained by the concept that the rate of burning is determined not by the whole of the combustion zone of the components, but only by that part of it which is close to the surface of the charge (see section 10,B).

The mixtures considered in this work have components which first vaporize and then react with one another. For sufficiently small values of d the ratio of the components in the gas phase is the same as in the original mixture, i.e. the reacting mixture is considerably diluted by the excess fuel and the burning rate is low¹.

However as the particle size of the oxidizer is increased only a portion of the original components succeeds in vaporizing and reacting within the boundary of the zone influencing the burning rate. At the same time the vaporization of the fuel, which is a strongly endothermic process, lags behind the vaporization of NH_4ClO_4 since the decomposition of NH_4ClO_4 is accompanied by the formation of an $\text{NH}_3 + \text{HClO}_4$ decomposition flame and takes place with the emission of heat; see section 10.

* NH_4ClO_4 was used with 'sieve' fractions of 320-400, 140-320, 100-140, 63-100, 50-63 and $< 50 \mu$ and also fractions of $\sim 17 \mu$ which were ground in a porcelain mill. The effective diameters of the two last fractions were calculated using the value of S_{sp} and were measured using apparatus PSKh-2.

¹Generally it is not possible to ignite a very finely divided ($d_{ox} \approx 5 \mu$) mixture of NH_4ClO_4 + perspex for $\alpha = 0.2$ at 5-100 atm.

Consequently as d_{ox} increases, the mixture reacting in the zone of influence is diluted less and less by the excess fuel. Hence the burning rate increases but only up to the point when there is a reduction in the heat release due to the decrease in the quantity of substance reacting in the zone of influence and to the increase in the heat lost in heating the fuel and oxidizer particles reacting a long way from the zone of influence. Thus for mixtures with a large excess of fuel the curve $u(d)$ must have a maximum.

On the other hand for stoichiometric mixtures both these processes (1 - decrease of fraction of substance reacting in zone of influence, 2 - change of composition of gas phase in zone of influence) with increase in d_{ox} operate in the direction of a reduction in burning rate, since for a stoichiometric mixture the delay in the vaporization of the fuel makes the reacting mixture less rich and lowers its temperature.

The following observation should be made. A fall in the burning rate occurs as d is decreased for a sufficiently large excess of fuel and for small values of d . Thus with a somewhat smaller excess of fuel in the range of small d a plateau can be expected, although its cause will be totally different from the one discussed previously in section 8,A. This may explain the presence of the plateau (rather long even at 50 to 70 atm) on the $u(d)$ curves for the Thiokol composition in the investigations of Ref.178 (Fig.31).

An anomalous curve $u(d)$ can evidently be observed also for mixtures with a very small percentage of fuel (i.e. with large excess of oxidizer). A considerable decrease in the dependence $u(d_{ox})$ was observed¹²³ as the flow of methane was decreased during the burning of a layer of particles of NH_4ClO_4 through which methane was blown. The ratio of the burning rate of the finest fraction investigated (74 to 105 μ) to that of the coarsest fraction investigated (297 to 420 μ) was as follows:

α	27.2	13.6	4.53	2.72	1.95
u_{fi}/u_{co}	1.0	1.22	1.25	1.25	1.27

Thus in this case there is a long plateau on the curve $u(d_{ox})$ for a very small percentage of fuel in that range of d where u increases significantly with decrease in d for mixtures not too far from stoichiometric.

In addition it was shown¹⁷³ that mixtures of finely divided NH_4ClO_4 with powdered volatile fuels, which contain a very small percentage of fuel, have a lower burning rate than pure NH_4ClO_4 (see also section 19). In other words the addition of a small percentage of fuel to finely divided NH_4ClO_4 lowers the burning rate. It is possible that with increase in d , other conditions being equal, this reduction will be less. If this is so, the dependence $u(d_{\text{ox}})$ will be anomalous, since with increase in d the absolute burning rate will increase somewhat. This has not yet been verified experimentally.

D DEPENDENCE $u(d)$ FOR POLYMODAL MIXTURES

The burning of systems using an oxidizer in the form of a mixture of two (or several) fractions of considerably different particle size is of great practical and theoretical interest.

If the burning rate were determined unambiguously by the magnitude of the specific surface of the components, then, for example, for a system containing 50% of a very coarse fraction of oxidizer, the burning rate u_{mix} would be approximately $(u_{\text{fi}} + u_{\text{co}})/2$, where u_{fi} , u_{co} are the burning rate for a system with finely divided oxidizer and a system with coarsely divided oxidizer respectively.

However, experiments have shown^{156, 168} that this simple relation is true for only part of the system (see composition 2 in Table 36).

For some of the other compositions (composition 3) u_{mix} is close to u_{fi} or even exceeds u_{fi} (composition 1 at 70 and 100 atm). On the other hand for other compositions u_{mix} is near to u_{co} (composition 4) or even less than u_{co} (composition 5 at 40 and 100 atm).

The relationship between u_{fi} , u_{mix} and u_{co} may be conveniently represented by the parameter Y where $Y = \frac{u_{\text{mix}} - u_{\text{co}}}{u_{\text{fi}} - u_{\text{co}}}$. For the cases considered above the value of Y is equal to

$$u_{\text{mix}} \geq u_{\text{fi}} \quad u_{\text{mix}} \leq u_{\text{co}} \quad u_{\text{mix}} = \frac{u_{\text{fi}} + u_{\text{co}}}{2}$$

$$Y \geq 1$$

$$Y \leq 0$$

$$Y = 0.5$$

TABLE 36

Burning rate of compositions based on NH_4ClO_4 with fine ($\sim 5\mu$), coarse (140 to 320 μ) and mixed (50% fine + 50% coarse) oxidizer

No. of composition	Fuel	Method of preparing mixture	α	Oxidizer particle size	u , mm/sec				
					10 atm	25 atm	40 atm	70 atm	100 atm
1	Polystyrene (< 100 μ)	Ungelatinized*	1	coarse	3.8	5.1	6.8	9.1	10.4
				mixed	4.8	7.2	9.1	12.2	15.1
				fine	4.9	7.4	9.3	12.0	14.6
				Y***	0.91	0.92	0.92	1.07	1.12
			0.5	fine	5.4	7.8	10.6	14.0	16.6
2	Polystyrene	Gelatinized*	0.7	coarse	4.2	6.6	7.6	10.3	12.1
				mixed	7.2	12.2	16.6	22.2	29.2
				fine	9.9	17.1	23.4	35.2	42.4
				Y	0.52	0.53	0.57	0.48	0.56
			0.35	fine**	6.2		14.0		26.5
3	Perspex	Ungelatinized	2	coarse	2.7	4.4	5.3	7.5	8.0
				mixed	4.9	7.9	10.6	12.9	15.8
				fine	5.4		10.7		16.2
				Y	0.82		0.98		0.95
			1	fine	7.0	11.1	14.5		22.8
4	Perspex ($\sim 3\mu$)	Ungelatinized	1	coarse	3.2	4.7	5.2		7.0
				mixed	4.0	5.3	5.8	7.3	7.5
				fine	5.7	8.1	9.1		12.7
				Y	0.32	0.18	0.15		0.09
			0.5	fine	3.3	4.2	3.9	4.0	6.0
5	Perspex	Ungelatinized	0.7	coarse	3.5	4.8	5.7		8.2
				mixed	4.0	5.2	5.6	6.3	7.4
				fine	4.5	5.4	6.2	7.8	8.7
				Y	0.50	0.67	-0.2		-1.6
			0.35	fine	Does not burn				

*The ungelatinized mixture was prepared by mixing the components in powder form. The gelatinized mixture was prepared in the same way, then treated with solvent (dichloroethane), mixed for 24 hours and dried. During gelatinization the fuel was spread as a film over the surface of the oxidizer particles.

**Data obtained by interpolation on curve $u(d)$.

$$Y = \frac{u_{\text{mixed}} - u_{\text{coarse}}}{u_{\text{fine}} - u_{\text{coarse}}}$$

The structure of the combustion zone must be considered to explain why in some cases u_{mix} is close to u_{fi} and in other cases close to u_{co} . Compositions with bimodal oxidizer are essentially inhomogeneous; there is a lattice of crystals of coarse oxidizer, the interstices between which are filled with a relatively homogeneous mixture of fuel and fine oxidizer with ratio of components equal to $\alpha/2$.

If the burning rate of this homogeneous mixture $(u_{\text{fi}})_{\alpha/2}$ is sufficiently high, a flame is propagated in the interstices between the coarse crystals of the oxidizer. The burning rate of a composition with mixed oxidizer u_{mix} is approximately equal to $(u_{\text{fi}})_{\alpha/2}$. At the same time if $(u_{\text{fi}})_{\alpha/2} \geq u_{\text{fi}}$, then $u_{\text{mix}} \approx u_{\text{fi}}$. The presence of the coarse oxidizer here only reduces the burning rate. On the other hand if $(u_{\text{fi}})_{\alpha/2}$ is close to u_{co} , then the presence of the coarse oxidizer can increase the burning rate. Finally if the homogeneous mixture in the interstices between the coarse crystals is unable to burn on its own or has a very low burning rate, then u_{mix} will be close to u_{co} and can even be less than u_{co} (but not less than $(u_{\text{co}})_{\alpha/2}$).

Thus the relationship between u_{mix} , u_{fi} and u_{co} is determined by the relationship between $(u_{\text{fi}})_{\alpha/2}$, u_{fi} and u_{co} . The general form of the curve $u(\alpha)$ is shown in Fig.32. Thus $(u_{\text{fi}})_{\alpha/2} > u_{\text{fi}}$, and $Y \geq 1$, can exist for $\alpha/2 > \alpha_2$, i.e. on the right-hand side of curve $u_{\text{fi}}(\alpha)$. The equality $(u_{\text{fi}})_{\alpha/2} \approx u_{\text{fi}}$ can exist for $\alpha > \alpha_2$. In this case the points $(u_{\text{fi}})_{\alpha/2}$ and u_{fi} lie to the left and right of the maximum respectively. Finally $(u_{\text{fi}})_{\alpha/2} < u_{\text{co}}$ is obviously satisfied for $\alpha \leq \alpha_1$.

Experiments were also made¹⁶⁸ with a mixed oxidizer containing 20% coarse and 80% fine fractions, as well as with a mixed oxidizer containing 50% coarse and 50% fine fractions. It was shown that $(u_{\text{mix}})_{20:80}$ was always almost equal to, but slightly less than, the burning rate of the homogeneous mixture $(u_{\text{fi}})_{0.8\alpha}$ in the interstices between the coarse crystals. This is in good agreement with the ideas proposed above.

14. DEPENDENCE OF BURNING RATE ON MIXTURE RATIO

The burning rate of condensed mixtures depends to a great extent on the oxidizer-fuel ratio, α .

The curve $u(\alpha)$ has a maximum at some value $\alpha = \alpha_{\text{max}}$ and on either side of this maximum the burning rate decreases, at first gradually and then more steeply. The side of the curve $u(\alpha)$ corresponding to excess fuel

stops sharply at some sufficiently small value of α ('rich' limit). On the other side there is also a 'lean' limit, for an oxidizer that is unable to burn on its own (e.g. KClO_4), whereas for oxidizers (e.g. NH_4ClO_4) which are able to sustain combustion on their own there is no 'lean' limit*.

A POSITION OF THE MAXIMUM BURNING RATE

It was shown in section 1,B that for gaseous mixtures with air and especially with oxygen mixtures the maximum burning rate was close to the stoichiometric (for air mixtures $\alpha_{u_{\max}} = 0.8$ to 1.1). The only exceptions were mixtures with hydrogen and carbon monoxide for which u_{\max} was displaced considerably in the direction of excess fuel. For hydrogen mixtures this displacement is associated with the fact that the velocity of the flame is determined to a considerable extent by the diffusion of active particles, in this case mainly hydrogen atoms, into the unburnt mixture.

For condensed mixtures with vaporizing components u_{\max} is close to the stoichiometric value (Refs. 164, 169, 141, 151, 175-177). Thus in investigations^{164,175} on finely divided mixtures of NH_4ClO_4 (or KClO_4) with polyformaldehyde, perspex, benzoic acid and bitumen u_{\max} (at $p < 100$ atm) occurred at $\alpha = 0.7$ to 1.0; data are given for a finely divided NH_4ClO_4 -perspex mixture in Fig. 33. A similar result was obtained¹⁷⁷ for mixtures of NH_4ClO_4 with a series of solid and liquid fuels (Table 37), and also in Ref. 176 for a layer ($\delta = 0.51$) of loose NH_4ClO_4 (250 to 540 μ) in powder form, through which was blown CH_4 , H_2 , C_2H_2 , C_2H_4 , C_3H_8 and C_5H_{12} . In particular the results obtained

TABLE 37

Dependence $u(\alpha)$ for NH_4ClO_4 mixtures with various fuels¹⁷⁷ ($p = 1$ atm abs)

Fuel	d_f, μ	d_{ox}, μ	$u, \text{mm/sec}$					
			$\alpha = 1.67$	$\alpha = 1.25$	$\alpha = 1.0$	$\alpha = 0.83$	$\alpha = 0.714$	$\alpha = 0.625$
Paraformaldehyde	< 75	102-250	0.865	0.895	0.955	<u>0.985</u>	0.91	0.90
Urotropine	< 100	102-250	0.56	0.77	0.93	<u>0.95</u>	0.91	0.86
Maleic anhydride	< 100	102-250	0.65	0.74	0.80	<u>0.79</u>	-	-
Methylmethacrylate (monomer)	Liquid	102-250	0.94	<u>0.97</u>	0.96	0.93	0.86	0.79
		250-500	0.83	0.90	<u>0.91</u>	0.87	0.82	0.77

NOTE: The maximum value is underlined.

*In section 19 it is shown that small additions of fuel to ammonium perchlorate result in extinction of burning for pressures at which pure NH_4ClO_4 burns perfectly steadily. In these cases there are two limits for the range of lean mixtures between which burning does not take place.

for methane and a $\text{CH}_4\text{-N}_2$ mixture were:

Mixture	$m, \text{ gm cm}^{-2} \text{ sec}^{-1}$				
	$\alpha = 2$	$\alpha = 1$	$\alpha = 0.667$	$\alpha = 0.5$	$\alpha = 0.4$
CH_4	0.111	<u>0.123*</u>	0.112	0.099	0.087
90% CH_4 + 10% N_2	0.096	<u>0.11*</u>	0.10	0.087	0.074
80% CH_4 + 20% N_2	0.080	<u>0.093*</u>	0.085	0.074	0.063

*See note to Table 37.

With increase in particle size of the components the maximum burning rate can be displaced in the direction of excess fuel (compare Fig.33 for a finely divided and Fig.34 for a coarse NH_4ClO_4 -perspex mixture and also the data for a finely divided and coarse NH_4ClO_4 -methacrylate mixture in Table 37).

Pressure has a slight influence on the position of u_{max} for mixtures based on NH_4ClO_4 . On the other hand for mixtures based on KClO_4 u_{max} is displaced considerably in the direction of excess fuel with increase in pressure, e.g. for a KClO_4 -urotropine mixture at 10 atm $\alpha_{u_{\text{max}}} \approx 0.9$ and at 50 atm $\alpha_{u_{\text{max}}} \approx 0.5$.

If u_{max} is close to $\alpha = 1$ for mixtures with vaporizing components, then in changing to a non-volatile fuel u_{max} is displaced significantly in the direction of excess fuel. Thus for mixtures based on KClO_4 at 30 to 100 atm the following value of $\alpha_{u_{\text{max}}}$ was obtained^{164,175}:

Dextrin	0.9
Graphite	0.4
Tungsten	< 0.1

where dextrin is a vaporizing fuel and tungsten is a non-volatile fuel, but with graphite the decisive role is played by the formation of CO on the surface of the particles with the subsequent burning of CO.

The burning of several mixtures with metal fuels at 1 atm abs was studied in Ref.179. In all cases u_{\max} was displaced in the direction of excess fuel. For the series of fuels Fe, Mn, Mo the greatest displacement of u_{\max} was observed for molybdenum, which is the least volatile (B.pt of Mn $\sim 2150^{\circ}\text{C}$, of Fe $\sim 2740^{\circ}\text{C}$ and of Mo $\sim 4800^{\circ}\text{C}$).

Thus the results obtained for mixtures based on KMnO_4 were

Fuel	Mn	Fe	Mo
% fuel at			
u_{\max}	45	55	76
q_{\max}	45	35	30
$\alpha_{u_{\max}}$	1.0	0.44	0.136*

An increase in the particle size of aluminium in the mixture $\text{Al-Fe}_2\text{O}_3$ displaces u_{\max} in the direction of excess fuel¹³⁹; thus for $d_{\text{Al}} \approx 4 \mu$ the maximum burning rate is at $\alpha \approx 0.8$, and for $d_{\text{Al}} \approx 160 \mu$ the burning rate continues to increase slowly at least up to $\alpha \approx 0.3$.

It is possible to explain these results for the position of the maximum on the curve $u(\alpha)$ by using the concept of the zone of influence. The value of α in the gas phase within the boundary of the zone of influence for mixtures with vaporizing components will be equal to the value of α in the original composition only for sufficiently finely divided mixtures. With an increase in the particle size of the components the value of α in the gas phase will change in the direction of an excess of the component which vaporizes more easily. For the mixtures considered this component is evidently the oxidizer (see section 6, 8, 10,B). Hence the gas phase within the boundary of the zone of influence contains more oxidizer than the original mixture, for coarse mixtures. Moreover, there is less fuel in the zone of influence for coarse mixtures than in the original mixture.

This effect can account for the displacement of the maximum burning rate u_{\max} in the direction of excess fuel with increase in particle size of the components. In fact with increase in the coarseness of the mixture, a greater excess of fuel is required in the original mixture in order to keep

*The value of $\alpha_{u_{\max}}$ is calculated on the assumption that the maximum heat of combustion is reached at $\alpha = 1$.

the composition of the gas phase in the zone of influence constant and close to that corresponding to the maximum rate of reaction.

The clearest explanation can be given of the phenomenon of the displacement of u_{\max} in the direction of excess fuel by considering the change from a volatile to a non-volatile fuel. With a less volatile fuel a greater excess is required in the zone of influence in order to ensure the same rate of reaction as calculated for example from the rate of consumption of oxidizer. The other case is equally important: with a vaporizing fuel there are high heat losses in heating it and in decomposing and heating the products of vaporization. Consequently the burning rate begins to fall significantly when the excess of the vaporizing fuel is not yet very high and especially so for a finely divided fuel. For a non-volatile fuel heat losses expended in vaporization are absent and thus only a very large excess of fuel begins to lower the burning rate.

B REDUCTION IN BURNING RATE DUE TO VARIATION OF MIXTURE RATIO FROM $\alpha_{u_{\max}}$

As the mixture ratio varies more from $\alpha_{u_{\max}}$, the composition corresponding to maximum burning rate, the curve $u(\alpha)$ at first falls rather gently and then more and more steeply. This fall in the burning rate may be characterized by the ratio u/u_{\max} for the given value of α/α_{\max} . Using the experimental data discussed in the previous section the following conclusions may be reached:

(1) In all cases an excess of fuel (in comparison with $\alpha_{u_{\max}}$) lowers the burning rate of coarse mixtures slightly and of finely divided mixtures considerably. In other words the value of u/u_{\max} (for a given value of $\alpha/\alpha_{u_{\max}} < 1$) for coarse mixtures is higher than for finely divided mixtures (Table 38). This result is obvious from the point of view of the concept of the zone of influence expressed at the end of the previous section. As the coarseness of the mixture is increased the amount of excess fuel that succeeds in vaporizing decreases and the ratio of the components in the gas phase approaches more closely to the stoichiometric value; with a non-volatile fuel an increase in d leads to a decrease in the heat lost in heating the excess fuel.

For excess oxidizer ($\alpha/\alpha_{\max} > 1$) the dependence of u/u_{\max} on particle size is less pronounced.

TABLE 38

Reduction of burning rate u/u_{\max} for a given variation $\alpha/\alpha_{u_{\max}}$ from the composition corresponding to maximum burning rate. Comparison of finely divided and coarse NH_4ClO_4 mixtures. The mean value of u/u_{\max} is taken over a pressure range 5-100 atm. In those cases where u/u_{\max} depends to a considerable extent on the pressure, values are given for some fixed value of p .

Fuel	$\alpha/\alpha_{u_{\max}}$	u/u_{\max}									
		2.0	1.6	1.4	1.2	1.0	0.8	0.6	0.4	0.2	
Perspex ^φ (~3 μ)(175)	$\bar{d}_{\text{ox}} = \sim 5 \mu$	0.72	0.79	0.85	-	1.0	0.86	-	-	-	
	$\bar{d}_{\text{ox}} = 140\text{--}320 \mu$	0.90	0.91	0.94	-	1.0	0.93	0.74 ^{φφ}	0.68 ^{φφ}	-	
Perspex* (175)	$\bar{d}_{\text{ox}} = \sim 5 \mu$	0.74	0.88	0.92	0.95	1.0	0.84	0.39	-	-	
	$\bar{d}_{\text{ox}} = 140\text{--}320 \mu$	0.89	0.91	0.92	-	1.0	0.93	0.83	-	0.61 ^{φφ}	
Polystyrene* (175)	$\bar{d}_{\text{ox}} = \sim 5 \mu$	-	-	0.93	-	1.0	-	0.76	0.46 ^{φφ}	-	
	$\bar{d}_{\text{ox}} = 140\text{--}320 \mu$	-	-	0.92	-	1.0	0.94	0.82	0.75 ^{φφ}	0.61 ^{φφ}	
C ₅ H ₈ O ₂ (monomer)** (177)	$\bar{d}_{\text{ox}} = 102\text{--}250 \mu$	0.875	0.93	0.97	0.99	1.0	0.955	0.84	-	-	
	$\bar{d}_{\text{ox}} = 250\text{--}500 \mu$	0.86	0.92	0.94	0.965	1.0	1.0	0.96	-	-	
Al + Fe ₂ O ₃ ^{φφ} (139)	$\bar{d}_{\text{Al}} \sim 4 \mu$	-	-	-	0.875	1.0	0.95	0.78	-	-	
	$\bar{d}_{\text{Al}} \sim 160 \mu$	-	0.89	0.98	-	1.0	-	0.99	-	-	

^φ Ungelatinized mixture.

* Gelatinized mixture.

^{φφ} $p = 100 \text{ atm}$.

** $p = 1 \text{ atm abs}$.

TABLE 39
Reduction of burning rate u/u_{\max} for a given variation $\alpha/\alpha_{u_{\max}}$ from the composition corresponding to maximum burning rate. Comparison of volatile and non-volatile fuels.

Mixture	Pressure, atm	u/u _{max}									Ref.
		$\alpha/\alpha_{u_{\max}} = 2.0$	1.6	1.4	1.2	1.0	0.8	0.6	0.4	0.2	
NH ₄ ClO ₄ -polypropylene (< 100 μ)	5-100	-	-	0.94	-	1.0	-	0.96*	0.89*	0.66*	175
KClO ₄ (fine)-dextrin (coarse)	5-100	-	0.85	0.88	0.90	1.0	0.90	0.76	-	-	175
KClO ₄ (fine)-graphite (1-3 μ)	5-100	-	0.58	0.73	0.87	1.0	0.94	-	-	-	175
Fe ₂ O ₃ (fine)-Al (~3 μ)	100	-	-	-	0.875	1.0	0.95	0.78	-	-	139
HClO ₄ (gas)-N ₂ -CH ₄	1 (210°C)	-	-	0.89	-	1.0	0.90	0.735	-	-	149
HClO ₄ (gas)-CO	1 (210°C)	0.735	0.81	0.84	-	1.0	0.955	-	-	-	149
NH ₄ ClO ₄ (140 to 320 μ)-perspex (~3 μ)	5-100	0.90	0.91	0.94	-	1.0	0.93	0.74*	0.68*	-	175
NH ₄ ClO ₄ (76 to 104 μ)-polystyrene (< 76 μ)	70	0.94	-	-	-	1.0	-	0.96	0.87	-	141
NH ₄ ClO ₄ (102 to 250 μ)-paraformaldehyde (< 75 μ)	1	0.875	0.89	0.92	0.975	1.0	0.95	0.73	-	-	177
NH ₄ ClO ₄ (102 to 250 μ)-urotropine (< 100 μ)	1	0.59	0.76	0.875	0.98	1.0	0.95	-	-	-	177
NH ₄ ClO ₄ (102 to 250 μ)-maleic anhydride (< 100 μ)	1	0.75	0.85	0.90	0.95	1.0	0.95	-	-	-	177
NH ₄ ClO ₄ (250 to 540 μ)-CH ₄	1	0.902	-	-	-	1.0	-	0.87	0.707	-	176
KClO ₄ (fine)-W (340 μ)	100	0.74	-	-	-	1.0	-	0.91	-	-	139

*p = 100 atm.

(2) A systematic dependence of u/u_{\max} on the volatility of the fuel has not been discovered, i.e. using coordinates $(u/u_{\max}, \alpha/\alpha_{u_{\max}})$ the data for condensed mixtures with a volatile and non-volatile fuel, for 'hybrid mixtures' e.g. particles of NH_4ClO_4 burning in a stream of methane, etc, and even for homogeneous gas mixtures are approximately grouped about the same curve (Table 39; see also Tables 6, 7 and 38).

However it should be emphasized that the variation of the composition from $\alpha_{u_{\max}}$, i.e. from the composition with maximum burning rate, is being considered. At the same time (as shown in the previous section) the value of $\alpha_{u_{\max}}$ is different for volatile fuels ($\alpha_{u_{\max}} \approx 1$) and non-volatile fuels ($\alpha_{u_{\max}}$ corresponds to a large excess of fuel). If the ratio $u/u_{\alpha=1}$ is calculated to show how the burning rate changes with the extent of the variation from the stoichiometric composition, then the effect of volatility will be very large; for instance for mixtures with perspex, when an excess of fuel is introduced, the value of $u/u_{\alpha=1}$ begins to fall rapidly and for mixtures with tungsten it will increase considerably right down to $\alpha \sim 0.1$.

(3) An excess of fuel reduces the burning rate less at a high initial temperature of the charge than at an ordinary initial temperature²¹⁶. In other words the value of u/u_{\max} for a given value of $\alpha/\alpha_{u_{\max}} < 1$ rises with increase of T_0 . A similar but less pronounced effect is observed for an excess of oxidizer. Thus for a gelatinized NH_4ClO_4 ($\sim 10 \mu$) + polystyrene mixture at 40 atm the following data were obtained:

$T_0, ^\circ\text{C}$	u/u_{\max}		$T_0, ^\circ\text{C}$	u/u_{\max}	
	$\alpha/\alpha_{u_{\max}} = 0.4$	$\alpha/\alpha_{u_{\max}} = 4.0$		$\alpha/\alpha_{u_{\max}} = 0.4$	$\alpha/\alpha_{u_{\max}} = 4.0$
15	0.21	0.43	~ 90	0.37	0.45
~ 60	0.22	0.42	135	0.41	0.57

15 DEPENDENCE OF BURNING RATE ON PRESSURE

The dependence $u(p)$ is a most important function* for the solid propellents used in rocket motors of various types. It is also of considerable importance for pyrotechnic mixtures.

For condensed mixtures (as well as for homogeneous explosive materials and homogeneous gaseous systems) the actual curve $u(p)$ is approximated by equation (2), $u = bp^v$. Equation (2) was first used at the end of the XIXth century by Vieille and since that time has been employed extensively. It is convenient for ballistic calculations. In particular the pressure in the combustion chamber of a rocket motor is given from theory by

$$p_c = \left(\frac{\rho b}{A} \frac{S}{S_{cr}} \right)^{1/(1-v)} \quad (100)$$

where ρ is the propellant density, A is the discharge coefficient, S is the burning area, and S_{cr} is the critical cross-sectional area of the nozzle. From (100) it is seen that combustion in the motor is stable only for $v < 1$ (see also Ref.194, etc). The use of the more complicated expressions $u = a + bp$, $u = a + bp^v$ and also (96) instead of (2) is not justified (see section 2,B); where necessary the actual curve $u(p)$ should be divided into several portions and the coefficients in equation (2) selected for each.

Most experimental data relating to the dependence $u(p)$ refer to the pressure range from 1 atm abs up to 100-200 atm. The very scanty data obtained for $p < 1$ atm abs (section E) and for pressures from several hundreds of atmospheres to several thousands of atmospheres (section F) will be considered separately.

A SHAPE OF CURVE $u(p)$

The shape of the curve $u(p)$ for condensed mixtures can be very varied as is also the case for homogeneous explosive materials; see section 2 and section 5. With increase in pressure the burning rate can behave as follows:

I It can rise monotonically. This type of curve $u(p)$ is observed both for systems with vaporizing components (Fig.35) and for systems where the fuel is non-volatile (Fig.36).

*In the literature on internal ballistics (see for example Ref.194) the function $u(p)$ is often called 'the law of burning' or the 'burning rate law'.

II It can rise and tend towards some constant value. This type of curve is often obtained for pyrotechnic mixtures (Fig.37, and curves 2 and 4 in Fig.38). However it is also sometimes observed (Refs.103, 141, 175) for mixtures with organic fuels (Fig.39).

III It can remain constant throughout the whole pressure range investigated (see curve 1 in Fig.38). This type of curve is relatively rare.

IV It can rise and then remain constant over a certain pressure range (plateau) and after that rise again (see curve 1 in Fig.40). Curves of this type are of considerable interest for solid propellents but are less frequently found than curves of type I.

V It can rise to some maximum value and then fall, sometimes with the extinction of burning. This type of curve is observed, although rather infrequently, both for mixtures with organic fuels (see curves 2 and 3, Fig.41) and pyrotechnic mixtures (see curve 3, Fig.38).

There is no sharp boundary between the types enumerated, and especially between the curves of type II and III; see Fig.37. Moreover all the experimental data relate to a limited pressure range. It is quite possible that by extending this range a curve of type II may change to a curve of type IV, etc.

The factors determining the form of the dependence $u(p)$ have as yet been investigated only to a small extent. The most natural explanation of the rise of burning rate with increase in pressure, in those cases where this occurs, is that the increase in pressure accelerates the reactions in the gas phase in the same way as in the case of volatile explosives and homogeneous gas mixtures*. However, while it is possible in a number of cases for gas mixtures and volatile explosives to relate the value of the exponent ν in the formula $m = bp^\nu$ with the order of the controlling reaction $n = 2\nu$, the value of ν is determined for condensed mixtures to a much lesser extent by the order of the controlling reaction and depends on many other parameters such as the particle size of the components, their volatility, their heat of vaporization, etc. It is usual to explain the absence of a burning rate dependence on pressure for non-volatile explosives on the assumption that the reaction in the condensed phase is the controlling reaction.

*For condensed mixtures theoretical models can be constructed (see Refs.202, 215, etc), in which the dependence $u(p)$ is associated with the change in the degree of dispersion for a change in pressure when the controlling reaction is in the condensed phase. This has not yet been investigated experimentally.

Such an explanation is also feasible for condensed systems (see Refs. 157, 250). However there are several examples such as burning of mixtures with a large excess of organic fuel, burning of mixtures with polymodal components and burning of some layer systems, for which the independence of the burning rate on pressure is obviously connected with other causes (see below).

The case where the burning rate falls with increase of pressure may also be connected with various causes. Thus in section 11 the fall in burning rate with increase of pressure ($\nu < 0$) was related to the formation of a crust of condensed residue on the surface of the strand in the presence of a controlling reaction in the gas phase. Systems with a large excess of organic fuel, for which on the $u(p)$ curves portions are observed with $\nu < 0$, will be examined below.

B EFFECT OF PARTICLE SIZE OF COMPONENTS ON DEPENDENCE $u(p)$

It was shown in section 13 that the particle size of the fuel and oxidizer can have a considerable effect on the absolute magnitude of the burning rate. Experiments show that the particle size of the components also has an effect on the shape of the curve $u(p)$.

For mixtures with organic fuels with a mixture ratio not far from stoichiometric, the particle size of the components has a relatively small effect on the form of the curve $u(p)$. However for finely divided mixtures u usually depends on p to a somewhat greater extent than for coarse mixtures. Consequently the value of ν in the equation $u = bp^\nu$ falls slightly, or remains approximately constant, with increase of the particle size of the components (Table 40).

For mixtures with a large excess of organic fuel the dependence of ν on d is variable: (1) for compositions 2 to 5 (see Table 40) the value of ν for finely divided mixtures is considerably higher than for coarse mixtures (i.e. ν falls significantly with increase of d); (2) for composition 7 the opposite effect is observed: the value of ν for finely divided mixtures is very much lower than for coarse mixtures at high pressures. An increase in ν with increase in d_{ox} is observed¹⁴⁶ for the composition 65% NH_4ClO_4 + 24% unsaturated polyester + 10% nitroglycerine:

d_{ox}, μ	40-53	53-74	74-88	88-105	105-147	147-297	297-500	500-710
ν	0.33	0.33	0.36	0.37	0.37	0.36	0.42	0.45

TABLE 40

Effect of NH_4ClO_4 particle size on the value of ν in the equation $u = b p^\nu$
for mixtures with organic fuels

No. of mixture	Fuel	d_{ox}, μ	ν					
			$\alpha = 2$	$\alpha = 1$	$\alpha = 0.7$	$\alpha = 0.5$	$\alpha = 0.3$	$\alpha = 0.2$
1	Bitumen ¹⁷³	~15	0.61	0.59	0.53	0.52	-	-
		~120	0.56	0.53	0.48	0.50	-	-
2	Polystyrene (< 100 μ) (ungelatinized mixture) ¹⁷⁵	~6	-	0.50	0.50	0.56	-	0.91*
		~40	-	0.50	-	0.44	0.58	0.74
		140 to 320	-	0.51	0.52	0.47	0.49	0.60
3	Do, gelatinized mixture ¹⁷⁵	~6	-	0.67	0.71	0.68	-	0.81
		~40	-	0.61	-	0.50*	0.65	0.85
		140 to 320	-	0.53	0.50	0.49	0.56	-
4	Polystyrene (< 100 μ) (ungelatinized mixture) ¹⁷⁰	~6	-	0.52*	-	-	-	0.83
		63 to 100	-	0.55*	-	-	-	0.58*
		100 to 140	-	-	-	-	-	0.58*
		320 to 400	-	0.59*	-	-	-	-
5	Perspex (~3 μ) (ungelatinized mixture) ¹⁷⁰	63 to 100	-	-	0.36* ($\alpha = 0.6$)	0.69 ($\alpha = 0.4$)	-	1.08*
		100 to 140	-	0.33	0.36* ($\alpha = 0.6$)	0.41 ($\alpha = 0.4$)	-	0.83*
6	Do ¹⁷⁵	~6	0.44	0.36*	0.38*	-	-	-
		140 to 320	0.45*	0.37	0.40	-	-	-
7	Do, gelatinized mixture ¹⁷⁵	~6						
		(5 to 25 atm)	0.53	0.55	0.50	0.49	0.6 $\nu = 0.6$	-
		(25 to 40 atm)	0.53	0.55	0.36	0.0		-
		(40 to 100 atm)	0.53	0.52	-0.24	-0.15		-
		140 to 320						
		(5 to 25 atm)	0.66	0.42	0.42	0.43	-	-
		(25 to 100 atm)	0.48	0.56	0.42	0.54	-	-

*In the pressure range 40 to 100 atm; in the other cases, except for mixture 7 - in the range 5 to 100 atm.

The independence, or slight dependence, of the value of ν on d_{ox} for compositions close to stoichiometric is unexpected and is in fact rather surprising. It would be expected for finely divided mixtures, where the influence of the kinetic factors is greater, that the dependence of u on p would be greater. There is as yet no satisfactory explanation why this is not observed, or is scarcely observed, experimentally.

On the other hand, the differences in the value of ν for finely divided and coarse mixtures with a large excess of fuel are in many ways more readily understood (see the following section).

It is necessary to deal separately with compositions with mixed, i.e. coarse + fine, oxidizer (section 13). But the burning rate of such mixtures in all cases rises monotonically with increase in pressure and, moreover, on the curves $u(p)$ there are not infrequently portions where the value of ν_{mix} is considerably higher or considerably lower than the value of ν_{fi} and ν_{co} corresponding to the finely divided and coarse oxidizer respectively. Thus for example the following values of ν (close to $p = 40$ atm) were obtained¹⁶⁸ for a gelatinized NH_4ClO_4 + polystyrene mixture, $\alpha = 1$ (mixture I); ungelatinized NH_4ClO_4 + polystyrene mixture, $\alpha = 0.5$ (mixture II); and gelatinized NH_4ClO_4 + perspex mixture, $\alpha = 1$ (mixture III):

Mixture	I	II	III
ν_{co}	0.55	0.47	0.41
ν_{mix}	0.75	0.57	0.18
ν_{fi}	0.68	0.56	0.54

These results are ascribed to the fact that the burning rate of compositions with mixed oxidizer u_{mix} is usually not the mean of the burning rates u_{fi} and u_{co} for the finely divided and coarse compositions respectively (see section 13). If at low pressure u_{mix} is close to u_{co} , but at high pressure close to u_{fi} , then evidently $\nu_{mix} > \nu_{fi}$ and $\nu_{mix} > \nu_{co}$. In the opposite case ν_{mix} will be lower than ν_{fi} and ν_{co} .

So far mixtures with vaporizing components have been considered. For mixtures with non-volatile fuels, the dependence¹³⁹ of u on p is greater for coarse mixtures and smaller for finely divided mixtures (Table 41).

TABLE 41

Effect of particle size of fuel on the value of exponent ν in the equation $u = bp^\nu$ for mixtures of oxidizer + metal¹³⁹

Mixture	α	ν for particle size of fuel, μ					
		0.1	2.7	19	160	340	550
20% $KClO_4$ + 80% W	~0.45	-	0.21	-	-	0.53	-
10% $KClO_4$ + 90% W	~0.20	-	0.23	0.20	0.42	0.40	0.37
5% $KClO_4$ + 95% W	~0.10	-	0.20	-	-	0.33	-
75% Fe_2O_3 + 25% Al	~1	0.078	-	-	0.14	-	0.26

For the $KClO_4$ -W and Fe_2O_3 -Al mixtures studied¹³⁹ this can be related to the mechanisms transferring oxidizer to the surface of the fuel particles through a layer of liquid residue (KCl, Fe and others, see section 8,B).

C EFFECT OF OXIDIZER/FUEL RATIO ON DEPENDENCE $u(p)$

The oxidizer/fuel ratio has a marked effect on the dependence $u(p)$ and in particular on the value of ν in the equation $u = bp^\nu$. Three types of $\nu(\alpha)$ curves were observed for the mixtures studied¹⁷⁵, almost exclusively in the range $0 < \alpha \leq 1$, i.e. for excess fuel.

Type I The magnitude of ν increases with increase in excess fuel, i.e. with decrease in α . This type of $\nu(\alpha)$ curve is observed for very many mixtures (see compositions 2 to 5 in Table 40 and Fig.42a). The $\nu(\alpha)$ curve for coarse mixtures and small values of α is located considerably below that for finely divided mixtures (see data for mixtures 2 and 4 in Table 40).

Type II The magnitude of ν decreases with increase in excess fuel. This type of curve is observed for a finely divided mixture of NH_4ClO_4 with perspex, especially at high pressures (see composition 7 in Table 40). A similar effect was observed for finely divided mixtures of NH_4ClO_4 with polyformaldehyde (PFA) and urotropine. Thus for example in the pressure range 70 to 100 atm the following values of ν were obtained¹⁷⁵:

α	ν		α	ν	
	PFA	Urotropine		PFA	Urotropine
1.0	0.53	0.72	0.50	0.0	-
0.75	0.57	-	0.25	-	0.0
0.65	-	0.80			

Type III The value of ν increases slightly with decrease in α and then passes through a maximum and begins to fall as in Fig.42b for a KClO_4 -W mixture. A maximum in the curve $\nu(\alpha)$ was also obtained for a KClO_4 -graphite mixture.

The dependence of the value of ν on α is connected with the dependence on pressure of the shape of the curve $u(\alpha)$ and on the position of the maximum on the curve $u(\alpha)$.

(1) If the position of u_{\max} and the form of the curve $u(\alpha)$ remain unchanged with increase in pressure (Fig.43a), then the exponent ν generally does not depend on α .

(2) If with increase in pressure u_{\max} is displaced in the direction of excess fuel ($\alpha_{u_{\max}}$ decreases with increase of pressure) (Fig.43b), then the value of ν increases with increase of excess fuel (curve $\nu(\alpha)$ type I).

(3) On the other hand if u_{\max} is displaced with increase in pressure towards the stoichiometric value or excess of oxidizer (Fig.43c), the value of ν falls with decrease of α (curve $\nu(\alpha)$ type II).

(4) If the curve $\nu(\alpha)$ becomes increasingly steeper with increase in pressure (Fig.43d), then ν has a maximum value (curve $\nu(\alpha)$ type III).

In practice the form of the curve $u(\alpha)$ and the position of u_{\max} may change simultaneously. Some experimental data in Table 42 show that the form of the curve $u(\alpha)$ is characterized by the magnitude u/u_{\max} for a given value of $\alpha/\alpha_{u_{\max}}$ (the flatter the curve $u(\alpha)$, the more nearly u/u_{\max} approaches unity).

For mixtures of NH_4ClO_4 with polystyrene, polypropylene and urotropine the curve $u(\alpha)$ becomes flatter ($u/u_{\max} \rightarrow 1$) with increase in pressure. Consequently on the side of excess fuel this leads to an increase in ν as α decreases (curve $\nu(\alpha)$ type I).

TABLE 42
Reduction of burning rate with increase of excess fuel (compared with $\alpha_{u_{max}}$) for NH_4ClO_4
mixtures at various pressures 175

d_{ox}, μ	Fuel	d_F, μ	$\alpha/\alpha_{u_{max}}$	u/u_{max}					
				5 atm	10 atm	25 atm	40 atm	70 atm	100 atm
~5 140 to 320	Polystyrene	<100	0.4	0.52	0.58	0.61	0.68	0.72	0.81
	"	<100	0.4	0.59	0.69	0.78	0.81	0.84	0.93
~40	Polypropylene	<100	0.4	-	0.73	0.83	0.68	-	0.89
~40	Urotropine	Finely divided	0.4	0.46	0.46	-	0.54	-	0.62
~5	Perspex	Gelatinized mixture	0.7	-	-	-	-	0.71	0.55
~5	"	"	0.6	-	-	-	-	0.42	0.36
140 to 320	"	"	0.4	-	0.61	0.75	0.75	-	-

On the other hand for a gelatinized mixture of finely divided NH_4ClO_4 with perspex the curve $u(\alpha)$ becomes steeper as the pressure increases, i.e. u/u_{\max} falls with increase of pressure. Consequently the value of ν falls with increase in excess of fuel (curve $\nu(\alpha)$ type II).

It is found that for the ungelatinized NH_4ClO_4 -polystyrene mixture and also for the KClO_4 -dextrin, KClO_4 -urotropine mixtures u_{\max} is displaced in the direction of excess fuel with increase in pressure, consequently ν increases as $\alpha \rightarrow 0$. On the other hand for a gelatinized mixture of finely divided NH_4ClO_4 with perspex u_{\max} is displaced in the direction of the stoichiometric mixture (from $\alpha \approx 0.8$ at $p = 5$ to 40 atm up to $\alpha \approx 1$ at $p = 70$ to 100 atm). This produces a reduction in ν for $\alpha \rightarrow 0$.

When explaining the positive or negative sense of the dependence of ν on α it is useful to consider how excess fuel affects the burning rate at low and high pressures. If the excess is large enough to reduce the burning rate perceptibly, and if the burning rate is reduced to a greater extent at low pressures and to a smaller extent at high pressures, then the value of ν will increase for $\alpha \rightarrow 0$ (curve $\nu(\alpha)$ type I). This corresponds to a fuel that is not too volatile, or not very finely divided. At low pressures, where the zone of influence is wide, the excess of such a fuel vaporizes completely or to a significant extent and thus greatly reduces the burning rate. At high pressures, where the zone of influence becomes narrower, a smaller proportion of the excess fuel vaporizes and the burning rate is reduced to a lesser extent.

On the other hand if the fuel properties are such that an excess reduces the burning rate to a lesser extent at low pressures and to a greater extent at high pressures, then the value of ν will fall for $\alpha \rightarrow 0$ (curve $\nu(\alpha)$ type II).

D EFFECT OF INITIAL TEMPERATURE, NATURE OF COMPONENTS AND ADDITIVES ON DEPENDENCE $u(p)$

In the literature there is not much information on these variables.

It is obvious that if the burning rate increases to a greater extent at high pressures and to a lesser extent at low pressures with increase in initial temperature or increase of some additive, then the dependence $u(p)$ becomes stronger (ν increases). On the other hand, when the burning rate increases to a greater extent at low pressures and to a lesser extent at high pressures, the dependence $u(p)$ becomes weaker (ν decreases). For additives which

decrease the burning rate, the dependence $u(p)$ becomes stronger (ν increases) in those cases where the additive is more effective at low pressures and is less effective at high pressures.

The effect of initial temperature on the value of ν for a composition based on NH_4NO_3 (with $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ as catalyst) is given in Ref.181. In this case the value of ν increases very slightly with increase in T_0 :

$T_0, ^\circ\text{C}$	-60	+15.6	+76
ν	0.384	0.388	0.416

Addition of copper chromite or SiO_2 to an NH_4ClO_4 -polyurethane binder-Al composition increases ν considerably¹⁸⁵; for the original composition $\nu \approx 0.11$, for the composition with 1% SiO_2 $\nu \approx 0.31$, and for the composition with 1% copper chromite $\nu \approx 0.51$.

The initial temperature and additives have a particularly marked effect in those cases where there is a plateau or especially if there is a part when $\nu < 0$ on the original curve $u(p)$.

The burning of a gelatinized NH_4ClO_4 ($\sim 5 \mu$) + perspex mixture, $\alpha = 0.5$, was studied²¹⁶. At 20°C the curve $u(p)$ for this mixture has a maximum at $p \approx 20$ atm and burning is extinguished above 40 atm (Fig.44). With an increase in T_0 to 75°C the burning rate increases up to ~ 40 atm, and then remains practically constant (at least up to 100 atm). Finally at 150°C the burning rate increases monotonically with increase of pressure over the range 5 to 100 atm (ν_5 to 100 atm ≈ 0.52).

A gelatinized NH_4ClO_4 ($\sim 5 \mu$) + perspex mixture, $\alpha = 0.6$, which has a maximum in the curve $u(p)$ at ~ 25 atm was modified¹⁷⁵ by addition of a less volatile fuel (polystyrene, wood charcoal) or a catalyst (Cu_2O). In each case the form of the curve $u(p)$ changed significantly; at 25 to 100 atm the burning rate no longer decreased but increased (Fig.45). A similar result was obtained¹⁴¹ for an addition of carbon black to an NH_4ClO_4 + paraformaldehyde mixture.

The experimental results^{141,175,185} discussed are in good agreement with the concept (see section 8,C) of the simultaneous occurrence of homogeneous reaction in a mixture of vaporization products of NH_4ClO_4 and the basic fuel

and heterogeneous reaction at the particles of the additive; the vaporization of the polystyrene is accompanied by the formation of soot particles.

The nature of the components can have a marked effect on the burning rate and the form of the dependence $u(p)$. However it is still not clear to what extent this is associated with the thermodynamic parameters of a given component (heat of vaporization, specific heat, temperature transfer coefficient, enthalpy) and to what extent with the chemical structure of the substance under investigation. So far these problems have scarcely been investigated.

Compositions based on KClO_4 show a much greater dependence $u(p)$ than compositions based on NH_4ClO_4 . Thus it was shown¹⁷³ that for oxidizer + bitumen compositions ($\alpha = 0.75$) the value of ν for NH_4ClO_4 is 0.51 to 0.55 and for $\text{KClO}_4 \sim 0.78$.

E DEPENDENCE $u(p)$ FOR $p \leq 1$ ATM ABS

Experimental data for the range $p \leq 1$ atm abs are very scanty and relate only to mixtures of oxidizers with organic fuels, whereas there are practically no data on the dependence $u(p)$ for pyrotechnic mixtures, although this pressure range is their usual working range.

For the systems oxidizer - organic fuel at low pressures the dependence $u(p)$ becomes considerably greater than at medium pressures.

For several such systems the dependence $u(p)$ at $p \leq 1$ atm abs approaches $u = bp$ (see Table 43 and also Fig.46)*.

The dependence $u = bp$ (at $p \leq 1$ atm abs) was also obtained¹⁹⁷ for a series of compositions with volatile components.

An increase of ν with decrease in pressure was observed¹⁵¹ for systems with volatile components, though ν does not increase up to unity, but to 0.70-0.75 (Table 44).

The strong dependence $u(p)$ for systems with volatile components at low pressures is usually ascribed (as in Refs.195, 197) to the fact that under these conditions the mixing of the components is completed in the preheating zone and burning takes place in the kinetic regime (section 8,A), similar to the burning of homogeneous volatile explosives. It is seen from section 2,B that in this case $\nu \approx 1$.

*The dependence $u = bp$ is characteristic of volatile explosives (Table 16).

TABLE 43

Value of coefficients ν and b in formula $u = bp^\nu$ for some mixtures
at near atmospheric pressures

Oxidizer	d_{ox}, μ	Fuel	α	ν	$b, \text{mm sec}^{-1} \text{atm}^{-1}$	Pressure range, atm	Ref.
NH_4ClO_4	10 to 20	Trotyl (TNT)	1	1.0	0.78	0.5 to 3.0	195
		Bitumen	1	1.0	1.4	0.2 to 1.0	195
	200	Bitumen	1	~ 0.7	~ 0.9	0.3 to 1.0	195
KClO_4	10 to 20	Bitumen	1	1.0	0.76	0.2 to 1.0	195
NH_4ClO_4	76 to 104	Paraformaldehyde	1	1.0	0.7	0.1 to 1.0	103
	-	Paraformaldehyde	2.8	1.0	0.7	0.1 to 1.0	109
		Polystyrene-polyester binder (20%)	-	1.0	1.02	0.2 to 1.0	196

TABLE 44

Values of exponent ν (in formula $u = bp^\nu$) at various pressures
for NH_4ClO_4 -polyester composition¹⁵¹

% NH_4ClO_4 / % binder	d_{ox}, μ	ν							
		0.2 atm abs	0.4 atm abs	0.7 atm abs	1.0 atm abs	2.0 atm abs	4.0 atm abs	7.0 atm abs	10 atm abs
75/25	40.6	0.7	0.7	0.69	0.68	0.67	0.60	0.48	0.40
70/30	40.6	0.7	0.7	0.66	0.64	0.63	0.47	0.43	0.42
75/25	75	0.72	0.67	0.65	0.64	0.64	0.59	0.51	0.47
70/30	75	0.75	0.68	0.66	0.66	0.66	0.54	0.3	0.27
70/30	120	0.7	0.7	0.69	0.68	0.64	0.58	0.56	0.56

However, this point of view is not in complete agreement with experiment. In particular, the concept of the complete mixing of the components in the preheating zone is not in agreement with the fact that during burning in a vacuum the extent of combustion decreases and the probability of dispersion increases. It was shown⁹⁸ that for stoichiometric mixtures of $\text{KClO}_4 + \text{Zr}$ and $\text{KClO}_4 + \text{W}$ at $p \approx 10^{-2}$ mmHg the extent of combustion of the metal amounts to $\sim 7\%$ for Zr and $\sim 12\%$ for W.

In addition, the concepts discussed predict that the following law should be observed: as the particle size of the components is increased, the pressure (or more accurately the burning rate) should decrease, and consequently the dependence $u(p)$ should become large. However, this law is not observed experimentally (see Table 44).

F DEPENDENCE $u(p)$ AT VERY HIGH PRESSURES

The dependence $u(p)$ in this range has been studied only in a constant pressure bomb⁴² at $p \leq 1000$ atm and in a variable pressure bomb⁴⁴ at $p \leq 4000$ atm. These experiments showed that the dependence $u(p)$ at very high pressures can be essentially different from that at $p \leq 100$ to 200 atm (Fig.4.7):

(a) For mixtures 1, 2, 7 (Fig.4.7) the dependence $u(p)$ in the range $p \approx 300$ to 1000 atm becomes considerably greater than in the range $p \leq 100$ to 200 atm.

(b) For mixtures 1, 2, 3, 7 (in the range 200 to 1000 atm) and also for mixture 4 (in the range 1000 to 4000 atm) the dependence $u(p)$ becomes almost one of direct proportion.

(c) For mixtures 5, 7 and especially 6 at sufficiently high pressures the dependence $u(p)$ becomes considerably less.

For mixture 7 the form of the dependence $u(p)$ may be followed over a very wide range of pressures: from ~ 0.5 atm abs to 4000 atm (Fig.48).

The curve in this case shows four distinct portions; the dependence $u(p)$ is linear* at low pressures (< 1 atm abs; portion 1) and at high pressures (600 to 2000 atm; portion 3), but it is slightly curved at medium pressures (portion 2) and at ultra-high pressures (portion 4). The available data at high and ultra-high pressures are very sparse at present, but they are nevertheless of great theoretical interest.

The decrease in the dependence $u(p)$ at high pressures is more easily understood. The increase in the burning rate with increase in pressure is connected with the increase in the reaction rate in the kinetic zone close to the 'tips' of the flame (see sections 9, 10). Consequently as the pressure increases, the reaction zone approaches closer and closer to the very point of the 'tip' of the flame, and this results in an increase in the lateral removal of heat used to heat that portion of the components which reacts outside the zone of influence. Thus, at sufficiently high pressures, the dependence $u(p)$ must become less.

Merely qualitative expressions and such sparse experimental data are insufficient to confirm that the dependence $u(p)$ is less at several thousands of atmospheres and that the mechanism discussed is correct.

It is more difficult to explain why the dependence $u(p)$ in the transition from medium to high** pressures becomes more pronounced for a series of mixtures (but not for all of them).

*The slope of the straight line $u(p)$ at low pressures is considerably greater than at high pressures; the value of b in equation $u = bp$ is $\sim 0.78 \text{ mm sec}^{-1} \text{ atm}^{-1}$ at low pressures and $\sim 0.115 \text{ mm sec}^{-1} \text{ atm}^{-1}$ at high pressures.

**Only the case of mixtures of the NH_4ClO_4 (or NH_4NO_3) - trotyl (TNT) type seems comparatively easy to explain, where both components are capable of self-sustained combustion and for both the dependence $u(p)$ is close to linear in the high pressure range.

16 DEPENDENCE OF BURNING RATE ON INITIAL TEMPERATURE

The burning rate of condensed mixtures increases monotonically with increase in the initial temperature T_0 in the same way as the burning rate of homogeneous gas mixtures (see section 1,D) and volatile explosives (see section 2,C). Consequently the shape of the curve $u(T_0)$ is simpler than those of the curves $u(p)$ and $u(d)$.

The dependence $u(T_0)$ may be characterized (as in section 1,D and section 2,C) using the temperature coefficient

$$\beta = \frac{1}{u} \frac{du}{dT_0} = \frac{d \ln u}{dT_0} \approx \frac{d \ln m}{dT_0} \text{ deg}^{-1}.$$

Thus if T_0 is increased by one degree and the burning rate increases by one per cent, then $\beta = 10^{-2} \text{ deg}^{-1}$ and so on. If for a temperature range T_{02} to T_{01} the experimental points in the coordinates $\ln u, T_0$ are grouped with sufficient accuracy around a straight line, then for this range $\beta = \text{constant} = \tan \phi = (\ln u_2/u_1)/(T_{02} - T_{01})$, where ϕ is the angle of the slope of this line with the axis of T_0 . If the range of T_0 is too wide, then it may be divided into several parts and the value of β determined for each part.

It was shown in section 1,D that for gas mixtures the value of β falls with increase of T_0 . On the other hand, for nitroglycerine powder (see section 5) β was observed to increase with T_0 , particularly over the interval 0 to 40°C. For condensed mixtures, it is often possible over a quite wide range of T_0 to take $\beta \approx \text{constant}$ (Fig.49). However for some mixtures β increases sharply with increase of T_0 (see Fig.50 and Table 45).

The temperature coefficient can also depend on pressure. In chapter I it was shown that for volatile explosives, and also for nitroglycerine powder, a significant decrease of β is observed with increase of pressure; thus, for example, for nitroglycerine powder⁴⁵ the value of β decreases on increasing the pressure from 10 to 45 atm by a factor of three - from $12 \cdot 10^{-3}$ to $4 \cdot 10^{-3} \text{ deg}^{-1}$. The relationship $\beta(p)$ for condensed mixtures has been investigated for only a few mixtures. Usually β falls slightly with increase of pressure. Thus, for example, for a NH_4ClO_4 ($\sim 10 \mu$) + bitumen mixture ($\alpha = 1$),

$$\beta_{1 \text{ atm abs}} = 1.7 \cdot 10^{-3} \text{ deg}^{-1} \quad \text{and} \quad \beta_{22.5 \text{ atm abs}} = 1.4 \cdot 10^{-3} \text{ deg}^{-1}$$

were obtained⁴⁵ for the range 20 to 90°C. In a few cases the decrease in β with increase of pressure is significant (see mixtures 1 and 2 of Table 46).

TABLE 45

The dependence $u(T_0)$ for the composition NH_4NO_3 + organic binder¹⁸¹

$\Delta T_0, ^\circ\text{C}$	$\beta \cdot 10^3, \text{deg}^{-1}$				
	p = 28 atm	p = 42 atm	p = 56 atm	p = 70 atm	p = 140 atm
-60 to +15.6	2.53	2.47	2.52	2.44	2.41
15.6 to 76	3.0	3.01	3.35	3.73	3.73

Note: The composition examined contained 72.79% NH_4NO_3 , 9.79% polyester resin (Genpol A-20), 12.22% methacrylate, 2.22% styrene, 1.99% $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and 1% other additives. The value of β was calculated (by us) from the experimental points of the curve $u(T_0)$.

TABLE 46

The value of β for various mixtures at different pressures¹⁶⁵

Mixture No.	Components	$\beta \cdot 10^3, \text{deg}^{-1}$			
		1 atm	5 atm	10 atm	20 atm
1	KClO_4 (~10 μ) + W (~3 μ) $\alpha = 1.78$	4.43 (20 to 400°)	3.4 (20 to 200°)	2.5 (20 to 200°)	2.3 (20 to 200°)
2	85% KNO_3 + 15% wood charcoal	5.0 (20 to 300°)	-	3.1 (20 to 250°)	-
3	Black powder DRP-3	1.4 (50 to 300°)	-	2.8 (2 to 225°)	-

Note: Values in brackets () = range ΔT_0 in deg C.

However, cases are also possible where the temperature coefficient can increase with increase of pressure (see mixture 3 of Table 46 and also the dependence $\beta(p)$ over the interval 15.6 to 76°C in Table 45).

The existence of the dependence of the temperature coefficient on initial temperature and pressure makes it difficult to compare the values of β for different systems, since the experimental data are often related to different ranges of initial temperature and different pressures. Fortunately, for systems with organic fuels the dependence $\beta(p)$ at $p \geq 1$ atm is slight, although some data at $p < 1$ atm abs show that the value of β can increase significantly as the pressure is reduced.

A ORDER OF MAGNITUDE OF THE TEMPERATURE COEFFICIENT

It has been shown that, at atmospheric pressure for homogeneous mixtures of fuel gases with air, the magnitude of β usually lies within the range (1 to 2) 10^{-3} deg^{-1} (see Table 9), for volatile explosives between (3 to 7) 10^{-3} deg^{-1} (see Table 17) and for nitroglycerine powder between (2 to 16) 10^{-3} deg^{-1} (depending on the range of T_0).

For condensed mixtures the order of magnitude* of β is also 10^{-3} deg^{-1} .

For mixtures with organic fuels with a composition not too far from the stoichiometric, the value of β for finely divided mixtures usually lies between (1 to 2) 10^{-3} deg^{-1} , and for coarse mixtures between (2 to 3) 10^{-3} deg^{-1} .

Thus the temperature coefficient for mixtures with organic fuels lies in the same range as that for gas mixtures and is significantly lower than the temperature coefficient for ballistite powders. Only for very large excess of fuel does the value of β for systems of mixtures rise sharply from $3 \cdot 10^{-3}$ to $7 \cdot 10^{-3} \text{ deg}^{-1}$; see B below.

For mixtures with metals and wood charcoal which are not far from the stoichiometric, the value of β lies within the range (0.5 to 5) 10^{-3} deg^{-1} .

*Measurement of the temperature coefficient for condensed mixtures and particularly coarse ones is experimentally very difficult on account of its small value. Measurement of the value of a temperature coefficient near to $1 \cdot 10^{-3} \text{ deg}^{-1}$, to an accuracy of 20%, requires determination of the burning rates at temperature T_{01} and $T_{02} = T_{01} + 100^\circ\text{C}$, for example, to an accuracy of ~1%, which is close to the limits of accuracy of existing methods of measuring burning rate.

The suggestion has been made¹⁶⁵ that the value of β increases with increase in the boiling point of the metal. Thus, for stoichiometric mixtures based on Fe_2O_3 , the following results were obtained over the range 20 to 400°C:

Metal	Mg	Al	B
T, boiling point of metal, °C	1100	~2300	~2500
$\beta \cdot 10^3$, deg ⁻¹	0.7	2.2	3.4

The data for black powder will be examined in section 20.

B EFFECT OF OXIDIZER/FUEL RATIO ON VALUE OF β

This question has been studied in comparative detail only for mixtures with organic fuels.

A clear relationship was established for these²¹⁶: the curve $\beta(\alpha)$ has a minimum which approximately coincides with the position of the maximum burning rate (see Tables 47 and 48, and Fig.51). On both sides of the minimum the temperature coefficient increases substantially.

TABLE 47

Dependence $\beta(\alpha)$ for NH_4ClO_4 + polystyrene mixtures²¹⁶
 $p = 40 \text{ atm}$ $\Delta T_0 = 15 \text{ to } 140^\circ\text{C}$

d_{ox}, μ	d_f, μ		α						
			2.0	1.5	1.0	0.63	0.50	0.35	0.20
~10	Gelatinized mixture	$\beta \cdot 10^3$, deg ⁻¹	4.2	4.4	2.0	2.0	<u>1.3*</u>	3.0	8.3
		$u_{18^\circ\text{C}}$, mm/sec	10.5	13.5	20.2	23.8	<u>25.5</u>	16.7	5.3
	< 100	$\beta \cdot 10^3$, deg ⁻¹	3.5	4.4	1.8	-	<u>1.2</u>	-	3.4
		$u_{15^\circ\text{C}}$, mm/sec	-	6.9	9.0	-	<u>11.6</u>	-	7.5
140-320	< 100	$\beta \cdot 10^3$, deg ⁻¹	2.6	3.2	2.6	-	<u>1.8</u>	-	4.1
		$u_{15^\circ\text{C}}$, mm/sec	5.6	5.8	6.3	-	<u>6.5</u>	-	4.9

*The maximum value is underlined.

TABLE 48

Temperature coefficient for a mixture of NH_4ClO_4 + polyester binder¹⁵¹

$p = 1 \text{ atm abs}$

d_{ox}, μ		% oxidizer/% binder			
		80/20	75/25	70/30	65/35
~40	$\beta \cdot 10^3, \text{deg}^{-1}$	1.2 (27-147°C)	1.8 (27-157°C)	1.5 (27-167°C)	2.3 (97-167°C)
	$u_{20^\circ\text{C}}, \text{mm/sec}$	1.1	1.03	0.98	0.76
75	$\beta \cdot 10^3, \text{deg}^{-1}$	1.7 (27-177°C)	1.7 (37-167°C)	2.0 (37-207°C)	2.7 (77-187°C)
	$u_{20^\circ\text{C}}, \text{mm/sec}$	1.05	0.94	0.85	0.64

Note: If the empirical composition of the binder is taken as $\text{C}_2\text{H}_4\text{O}$, then the oxidizer/fuel ratios 80/20, 75/25, 70/30 and 65/35 correspond to the values $\alpha \approx 0.76, 0.56, 0.44$ and 0.35 respectively.

C EFFECT OF PARTICLE SIZE OF COMPONENTS ON VALUE OF β

For mixtures with organic fuels with near stoichiometric compositions, the temperature coefficient increases with increase of the particle size of the oxidizer (Table 49).

TABLE 49

Dependence $\beta(d_{\text{ox}})$ for a series of stoichiometric mixtures²¹⁶

Mixture	d_{ox}, μ	$\beta \cdot 10^3, \text{deg}^{-1}$	$T_0, ^\circ\text{C}$	p, atm
NH_4ClO_4 -bitumen	~10	1.4	20 to 90	22.5
	~1800	2.6	15 to 100	
KClO_4 -bitumen	~10	1.4	-40 to +70	40
	~1800	5.0	20 to 90	
NH_4ClO_4 -polystyrene (< 100 μ) (ungelatinized mixture)	~10	1.8	15 to 135	10
	140 to 320	2.6	15 to 164	
NH_4ClO_4 -perspex (gelatinized mixture)	~5	1.2	15 to 170	10
	100 to 140	2.6	15 to 180	

On the other hand the values of β_{fi} and β_{co} can approach one another for a sufficiently large excess of fuel or oxidizer and moreover β_{fi} can exceed β_{co} . Thus the results obtained for an ungelatinized NH_4ClO_4 + polystyrene ($<100 \mu$) mixture (see Table 47) were:

α	2	1.5	1.0	0.5	0.2
β_{co}/β_{fi}	0.74	0.73	1.45	1.50	1.20

A similar conclusion may be drawn from the data of Table 48.

If mixtures with non-volatile fuels are considered, no dependence of β on the particle size of the tungsten for a $\text{W} + \text{KClO}_4$ mixture ($\alpha = 0.76$) at 1 atm abs was found¹⁶⁵; for $d_w \approx 3, 40$ to 100 and 140 to 400μ the value of β in the range 20 to 300°C within the limits of the scatter of the results remained constant and equal to $\sim 3.1 \cdot 10^{-3} \text{ deg}^{-1}$.

* * *

In conclusion, the explanation for the experimental data discussed will be considered briefly.

The basic idea is that the value of the temperature coefficient β is determined by the effective temperature $T_{\text{eff}} = T_c$ in the controlling reaction zone; if T_c is high, then β is small and conversely if T_c is low then β is large^{45,47}. This is reflected in equation (7), $\beta = E/2RT_c^2$.

For coarse mixtures, whose composition is not far from stoichiometric, the main part of the heat evolved in the zone of influence is used to heat the particles reacting a long way from the zone of influence. Therefore the value of T_c is lower and the temperature coefficient correspondingly higher for coarse mixtures than for finely divided mixtures.

However, the difference in the values of T_c for coarse and for finely divided mixtures is smoothed out with an increase in the excess of one of the components, since in the zone of influence a smaller fraction of the excess component is able to vaporize for the coarse mixture than for the finely divided mixture. Consequently the values of β_{co} and β_{fi} approach one another and for a sufficiently large excess of one component it is possible that $\beta_{co} < \beta_{fi}$.

The dependence $\beta(\alpha)$ is now considered. The maximum of the equilibrium temperature of combustion T_e is close to $\alpha = 1$, although some deviation from $\alpha = 1$ may be related to the dissociation of the combustion products. For finely divided mixtures with volatile components the value of T_c is close to T_e . Therefore the positions of $u_{\max} = f(T_e)_{\max}$, β_{\min} and $(T_e)_{\max}$ coincide and are close to $\alpha = 1$ as in Fig.52 for a finely divided NH_4ClO_4 + polyformaldehyde mixture.

However for NH_4ClO_4 + polystyrene mixtures the vaporization of the fuel lags behind the vaporization of the oxidizer and is accompanied by the formation of carbon black. The burning of the carbon black particles takes place relatively slowly and cannot be completed within the boundary of the zone of influence. It is necessary to have a sufficient excess of fuel in the original mixture to ensure that the mixture reacting in the zone of influence does not contain excess oxidizer. Therefore for NH_4ClO_4 + polystyrene mixtures $u_{\max} = f(T_c)_{\max}$ and β_{\min} are in the region corresponding to considerable excess of fuel ($\alpha \approx 0.5$) and do not coincide with $(T_e)_{\max}$.

The slight dependence of the temperature coefficient on pressure (at $p > 1$ atm abs) obviously shows that complete combustion is achieved at low pressures for systems of mixtures and a further increase of pressure has little effect on the value of T_c . However there are cases where β increases with increase of pressure. That shown in Fig.44 where the burning rate falls with increase in pressure at ordinary temperatures can be understood relatively easily by the decrease in T_c caused by an unfavourable change in the mixture ratio in the zone of influence, and also by the increase in the role of heat losses, etc. Obviously β will increase with increase in pressure in this case.

17 EFFECT OF CATALYTIC ADDITIVES

The burning rate of condensed mixtures can be changed in the same way as for gaseous mixtures by introducing small amounts, not more than a few per cent, of additives.

Since the action of such additives on the burning rate is not explained in most cases by their effect on the heat of combustion, because many additives which increase the burning rate lower the heat of combustion, it is customary to call them catalysts. However it is not clear whether they are catalysts in the precise meaning of the word.

The data available in the literature, which are exceedingly sparse, show that additions of catalyst can change the burning rates of condensed mixtures by not more than a factor of two or three. This is considerably less than for gaseous mixtures, where introduction of 1-2% of additives can change the burning rate by a factor of 5 to 10 (see Tables 10 and 11).

Thus the effect of catalytic additives on the burning rate is very much less than the effect of catalysts on the rate of chemical reactions at low and moderate temperatures, where catalysts can change the rate by many orders of magnitude and tens of orders of magnitude. This is related to the general principle which states that it becomes increasingly difficult to change the rate of a reaction as the temperature at which the reaction takes place is raised.

Nevertheless catalytic additives can play an important role in combustion, and systems based on NH_4NO_3 are not, in general, used without catalysts because burning is not sufficiently stable. Moreover at ordinary temperatures pure NH_4ClO_4 and NH_4NO_3 can burn only at an elevated pressure (NH_4ClO_4 at $p > 30-40$ atm and NH_4NO_3 at a considerably higher pressure)*. Additions of catalyst enable NH_4ClO_4 and NH_4NO_3 to burn even at atmospheric pressure.

First, the data available in the literature on catalytic additions to systems based on NH_4NO_3 are considered. In most cases 2-3% ammonium bichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, is used as the catalyst^{180,181}. The most efficient catalysts are stated¹⁸² to be K_2CrO_4 and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. The high efficiency of K_2CrO_4 has been confirmed¹⁸³, although $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ was found to be considerably less effective (Table 50), but the investigations in Ref.183 were carried out at 1 atm abs, whereas those in Refs.180 and 181 relate to a pressure range of 30 to 300 atm. The action of Cr_2O_3 was also studied^{108,180}, but it was found that $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ has a much stronger effect than the equivalent concentration of Cr_2O_3 .

* NH_4NO_3 burns in a manometric bomb at $p > 130$ atm²³⁷. It was not possible to attain stable burning of NH_4NO_3 at $p < 1000$ atm in a constant pressure bomb.

TABLE 50

Burning rate of mixture NH_4NO_3 + 10% additive at atmospheric pressure¹⁸³

Additive	Relative density of charge, δ	u , mm/sec	m , $\text{gm cm}^{-2} \text{sec}^{-1}$
K_2CrO_4	0.5	1.73	0.086
$\text{K}_2\text{Cr}_2\text{O}_7$	0.5	1.33	0.066
$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	0.6	0.83	0.05
$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	0.5	0.32	0.016
$(\text{NH}_4)_2\text{CrO}_4$	0.5	0.23	0.012

Evaluation of the relative efficacy of additives is made difficult, since in Refs. 108, 180-183 the burning rate is not given for the same systems without additives. However, these data cannot be obtained at low temperatures, since mixtures based on NH_4NO_3 and especially pure NH_4NO_3 will not burn under these conditions.

Exceptions in this respect are the data¹⁸⁴ on the effect of additions of some surface-active substances on the burning rate of a composition based on NH_4NO_3 . Thus for example the results obtained for sodium dinaphthylmethane-disulphonate were:

Additive, %	0	0.1	1.0	2.0	3.0
$u_{p=50 \text{ atm}}$, mm/sec	0.97	1.17	1.50	1.58	1.57
$Z = \frac{u_{\text{with additive}}}{u_{\text{without additive}}}$	-	1.20	1.55	1.63	1.62

Additives used for accelerating the burning rate of NH_4ClO_4 and compositions based on it are: CuO (Ref. 120), copper chromite (85% CuO + 15% Cr_2O_3) (Refs. 120, 185, 187), Cu_2O (Refs. 173, 175), Fe_2O_3 (Ref. 120), SiO_2 (Ref. 185), Cu_2Cl_2 (Ref. 186), etc, and for retarding the burning rate LiF (Refs. 185, 187) is used.

The burning rate of NH_4ClO_4 -fuel mixtures with 1-2% additive could be changed by not more than 1.5 to 2 times. The burning of pure NH_4ClO_4 is greatly affected by the action of additives; it is possible to change its burning rate up to 3 to 4 times with 2-5% additive.

The literature data enable certain conclusions to be reached regarding the effect of catalytic additives.

(1) The effect of the additives is intensified by reducing the oxidizer particle size. Thus the composition 76% NH_4ClO_4 + 24% binder was studied¹⁸⁷; for $d_{\text{ox}} \approx 15$ and $\approx 80 \mu$ the respective burning rates at $p = 14$ atm were 8.4 and ~ 4.2 mm/sec. Addition of 1% copper chromite increased the burning rate (at 14 atm) of the finely divided composition 1.67 times and of the coarse composition 1.58 times. Addition of 1% lithium fluoride reduce the burning rate of the finely divided composition 1.7 times and of the coarse composition only 1.23 times.

(2) The effect of an additive is intensified by increasing the percentage of additive (within limits of 2 to 5%). Thus the results obtained¹⁸⁵ for a composition with 70% NH_4ClO_4 + 25% polyester-urethane binder + 5% Al were:

LiF, %	0	0.5	1.0	1.5	2.0
$u_{56 \text{ atm}}$, mm/sec	5.8	5.17	4.52	3.92	3.28
Z	-	0.89	0.78	0.68	0.57

Similar results for the addition of copper chromite are given in Ref.120 (Table 51) and in Ref.187 (Table 52).

(3) The efficacy of the additives depends on the pressure. For copper chromite and silica dioxide the effect becomes more marked as the pressure is increased (see Tables 51, 52).

TABLE 51

Influence of pressure on the efficacy of catalysts
on burning rate of pure NH_4ClO_4 (Ref.120)

Catalyst		Pressure, atm						
		50	60	70	80	90	100	150
No catalyst	u, mm/sec	6.3	7.2	8.2	8.9	9.5	10.2	12.3
3% copper chromite	u, mm/sec	11.1	17.1	23.2	27.4	30.7	33.6	43.6
	Z*	1.76	2.36	2.83	3.08	3.23	3.30	3.55
5% copper chromite	u, mm/sec	22.2	26.1	30	32.8	35.2	38	46.8
	Z*	3.52	3.60	3.66	3.68	3.71	3.73	3.81

Note: The numerical data are taken from graphs.

* $Z = u_{\text{with catalyst}} / u_{\text{without catalyst}}$.

TABLE 52

Influence of pressure on the efficacy of catalysts
on burning rate of composition
 NH_4ClO_4 -polyurethane binder-Al (Ref.185)

Catalyst		Pressure, atm			
		49	56	63	70
No catalyst	u, mm/sec	5.14	5.19	5.26	5.34
1% copper chromite	u, mm/sec	6.49	6.86	7.32	7.75
	Z*	1.26	1.32	1.39	1.45
1% SiO_2	u, mm/sec	8.35	8.72	9.0	9.3
	Z*	1.62	1.68	1.71	1.74

Note: The numerical data are taken from graphs.

* $Z = u_{\text{with catalyst}} / u_{\text{without catalyst}}$.

18 BURNING IN SYSTEMS CONSISTING OF PLANE OR CYLINDRICAL LAYERS OF FUEL AND OXIDIZER

Experiments have shown^{124,127,166} that combustion can be achieved in a system consisting of layers of any thickness of fuel and oxidizer* in contact with one another (layer system).

Various methods of manufacturing charges have been used depending on the properties of the components. When an organic polymer with satisfactory mechanical properties was used as the fuel, it was formed into a flat layer, or cylindrical tube into which the oxidizer was pressed. In other investigations a pellet was first formed by pressing and then the fuel in powder form was pressed at a low pressure into a hole drilled in the pellet. If both components were in powder form and the experiments were to be carried out at low densities the components were poured into a mould provided with a fine membrane, such as tracing cloth, which separated the components during the preparation of the charge and was then removed.

The charge was ignited at the upper end simultaneously along the whole length of the boundary of contact by means of a coil of nichrome wire in the experiments with organic fuels or by means of an igniter compound in the experiments with metal powders.

A flame was propagated from above down the surface of contact of the components. Wedge shaped indentations were formed in the fuel and oxidizer layers, inside which the combustion zone was located, and these moved along

*In the experimental investigations^{124,127,166} and the theoretical investigations⁵ the case where each of the components was incapable of sustaining combustion independently was investigated. The burning of NH_4ClO_4 in a perspex tube was examined in Ref.121. In this case the oxidizer was capable of self-sustained burning over a certain pressure range. It is shown in section 19 that in this case the diffusion flame on the surface of contact of the fuel and oxidizer greatly extends the range of stable burning. Experiments have shown, however, that in the pressure range where the burning of NH_4ClO_4 is stable in an inert casing the use of a fuel casing changes the burning rate slightly. It is, therefore, really the burning of pure NH_4ClO_4 in the presence of a 'pilot' flame at the edges of the charge.

with the flame. The velocity of propagation of the flame along the surface of contact of the components u attained a stationary value quite rapidly*.

The form of the indentation during burning was very sharply defined for those components such as perspex which do not melt before vaporizing and do not form a condensed residue. On the other hand, the shape of the indentation was distorted by the presence of a condensed residue for such components as KClO_4 , KClO_3 , BaO_2 and KMnO_4 . Thus the burning of systems with KClO_4 and KClO_3 is accompanied by the formation of large liquid drops of KCl ; from time to time the drops are ejected by the flow of gas and new ones are formed in their place. The burning of systems with BaO_2 and KMnO_4 is accompanied by the formation of a solid porous slag with a volume close to that of the original oxidizer.

The burning rate along the surface of contact in the case of layers of transparent fuels was measured by means of a photorecorder^{124,127} and in the case of layers of opaque components by means of ionization gauges or fine quartz filaments acting as light conductors leading out from the surface of contact¹⁶⁶.

A LIMITING CONDITIONS FOR BURNING

The limiting conditions for burning along the surface of contact of the components can be quite sharply defined. Thus in perspex tubes it was not possible to establish combustion (at $p \leq 40$ atm) for any one of the many nitrates investigated¹²⁴, although the calculated heat release for $\text{Pb}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ and especially for LiNO_3 is considerably higher than for BaO_2 or KMnO_4 , which burn well in perspex tubes even at 1 atm abs. This is possibly related to the fact that decomposition of nitrates does not liberate oxygen but the relatively inert nitrogen peroxide. Burning in contact with KClO_4 (at $p < 60$ atm) could not be established for those fuels (polyethylene-terephthalate, galalith, phenolformaldehyde resin, etc) which form a large

*This is naturally not the normal burning rate. Thus the mass burning rate should not be calculated in the usual way when considering the propagation of a flame along the surface of contact of the components. The linear and mass rate of vaporization of the fuel and, less accurately, of the oxidizer inside the indentation can be calculated (see section 6,C and section 9), but this rate is characteristic only of the formation of the indentation and not of the propagation of the flame along the surface of contact of the components. Moreover the burning rate u for ordinary disordered systems for $d > d_{\min}$ is also not the normal burning rate. However, the velocity of both processes will be denoted by the letter u and where necessary subscripts will be used.

TABLE 53

Ability of various oxidizers to burn in contact with aluminium

- +++ very vigorous burning sometimes with a loud noise;
 ++ vigorous burning;
 + burning of moderate intensity;
 ± feeble burning, often extinguished;
 - burning does not take place.

Oxidizer and its decomposition products	Q_{decomp} , kcal/mole O_2	p, atm (gauge)	Result
$KClO_4 \rightarrow KCl + 2O_2$	4.5	0	+++
$Ag_2O \rightarrow 2 Ag + 0.5O_2$	14	0	+++
$PbO_2 \rightarrow PbO + 0.5O_2$	24	0	+++
$2 KMnO_4 \rightarrow 2 MnO + K_2O + 2.5O_2$	33	0	+++
$BaO_2 \rightarrow BaO + 0.5O_2$	38	0	+++
$Ba(NO_3)_2 \rightarrow BaO + N_2 + 2.5O_2$	41.5	0	++
$MnO_2 \rightarrow MnO + 0.5O_2$	66	0	+
$CuO \rightarrow Cu + 0.5O_2$	75	0	++
$Co_2O_3 \rightarrow 2 Co + 1.5O_2$	100 100	0	±
		20	+
$PbO \rightarrow Pb + 0.5O_2$	104	0	+
$Fe_2O_3 \rightarrow 2 Fe + 1.5O_2$	130 130	0; 10	-
		20	+
$SnO \rightarrow Sn + 0.5O_2$	136 136	0	-
		20	+
$ZnO \rightarrow Zn + 0.5O_2$	166 166	0; 10	-
		20	+
$Cr_2O_3 \rightarrow 2 Cr + 1.5O_2$	182 182	0; 20; 40	-
		50	+

Note: Aluminium (powder) in the form of a cylinder of diameter 8 mm was surrounded by a coaxial layer of solid oxidizer with an external diameter of 22 mm; the density of both components was that of the powdered form.

amount of carbon residue during their thermal decomposition in the presence of oxygen.

For metal powders there is a limiting relative density of layer for which burning becomes impossible because of the extremely high heat transfer from the combustion zone into the interior of the fuel layer. The limiting relative density δ_{lim} is about 0.5 for tungsten powder (mean particle size $\sim 3 \mu$) in contact with $KClO_4$ at 20 atm.

The value of δ_{lim} depends on the size of the layer and the pressure. A limiting relative density is not observed for organic fuels, i.e. burning takes place even for a solid plate ($\delta \approx 1$) of fuel. It is reasonable to relate this to their low thermal conductivity in comparison with that for metals.

On the other hand the effect of the nature of the oxidizer on its ability to burn in contact with aluminium or tungsten is exerted only through the change in the heat of combustion, although such startling discrepancies between the calculated and actual values of the ability to burn as found for organic fuels have not been observed. The data given in Table 53 show that the ability to burn for the systems under investigation decreases steadily with increase in the heat lost Q_{decomp} in the decomposition of the oxidizer, i.e. the amount required to liberate 1 mole of O_2 . As Q_{decomp} increases, the pressure increases and hence burning becomes possible.

B DEPENDENCE OF FLAME VELOCITY ON LAYER THICKNESS OF COMPONENTS

Experiments were carried out in which the thickness d of the layer of one of the components was varied whilst the thickness of the other was kept constant (the configuration of the charges is shown in Fig.53).

In all the cases investigated there is a plateau on the curve $u(d)$ for sufficiently large values of d (Figs.54, 55a, b)*.

This phenomenon is related to the presence of the zone of influence (see section 10,B); the burning rate changes with increase in the width of the combustion zone (resulting from an increase in d) only up to the point where the value of $d \cot \phi$, where ϕ is the angle of burning, becomes larger than the size of the zone of influence. Thus the dependence $u(d)$ can be used for evaluating the size of the zone of influence.

*A reduction of the dependence $u(d)$ for large values of d was also observed¹⁶⁶ for a core of aluminium powder in a coaxial tube of BaO_2 although a considerable scatter of the values of u was observed for small values of d for this system.

For small values of d the curve $u(d)$ can have various forms:

(1) For a perspex layer (Fig.55a) and a polyethylene layer (Fig.55b) between layers of $KClO_4$ and also for a BaO_2 layer between layers of perspex (curve 3 in Fig.54) the burning rate falls as d is reduced.

(2) For a $KClO_4$ layer between layers of perspex (curves 1 and 2 in Fig.54) the burning rate increases as d is reduced.

The reasons for the different shapes of the curve $u(d)$ for small values of d are still uncertain in many respects, but it is evident that the form of the curve $u(d)$ for a single layer at small values of d is determined by two competing processes:

(a) The total heat release is reduced with decrease in d for a single layer whereas the heat losses to the external layers remain approximately the same. Consequently the relative importance of the heat losses again increases*.

(b) The distance between the flame propagated along the left and right boundary of the layer decreases with decrease in d , and consequently the heat losses decrease inside the layer.

C DEPENDENCE OF FLAME VELOCITY ON PRESSURE

All the basic forms of the curves $u(p)$ known for the usual disordered systems were observed for the layer systems studied in Refs.127, 124 and 166.

(1) For the systems $KClO_4$ -perspex, polyethylene, polystyrene, vinyl plastic; $KClO_3$ -perspex; $Ba(NO_3)_2$ -Al; $KClO_4$ -W the burning rate increased monotonically with pressure over the pressure ranges investigated (see curves 1 and 2 in Fig.56 and curve 1 in Fig.57). The value of the exponent ν in the equation $u = bp^\nu$ for these systems is as follows:

<u>Oxidizer</u>	<u>Fuel</u>	<u>ν</u>	<u>Pressure, atm</u>
$KClO_4$	Polystyrene	~1.2	5 to 40
$KClO_3$	Perspex	1.06	20 to 125
$KClO_4$	Polyethylene	0.64	10 to 30
$Ba(NO_3)_2$	Aluminium	0.49	30 to 100
$KClO_4$	Polyvinylchloride	0.42	10 to 40

*On the other hand, for systems consisting of many layers, the number of which per unit length of charge increases with decrease in d , the total heat release in the zone of influence will increase as d is decreased, and thus the heat losses will decrease again.

For the KClO_4 -perspex system $v \approx 0.82$ was obtained for plane layers (5 to 40 atm), $v \approx 0.47$ for cylindrical layers (2.5 to 20 atm) and $v \approx 0.95$ for cylindrical layers (30 to 125 atm) (Refs. 124 and 127).

(2) The burning rate for the KMnO_4 -perspex (see curve 4 in Fig. 56) and KMnO_4 -W (see curve 2 in Fig. 57) systems increases only up to a certain pressure and then remains constant over a wide pressure range.

(3) The burning rate for the BaO_2 -perspex system first increases with increase in pressure, then passes through a maximum and begins to decrease (see curve 3 in Fig. 56).

In the same way as in the usual disordered mixtures, the increase in the velocity of propagation of the flame along the surface of contact of the components is related to the increase in the rate of the reactions in the kinetic zone close to the 'tip' of the flame.

The case where the burning rate of a layer system does not depend on the pressure over a certain pressure range has been observed only for KMnO_4 systems. A considerable amount of solid residue is formed in the decomposition of KMnO_4 . The flow of oxygen to the reaction zone through the layer of solid residue evidently cannot exceed a certain value (i.e. burning takes place in the diffusion regime), which results in the appearance of a plateau in the curve $u(p)$.

Finally, the case of the BaO_2 -perspex layer system, where the burning rate passes through a maximum, is probably also associated with a solid residue; an alternative hypothesis, which cannot yet be discarded, suggests¹²⁷ that a reversal of the reaction $\text{BaO}_2 \rightleftharpoons \text{BaO} + 0.5\text{O}_2$ takes place, and thus an increase in pressure retards the decomposition of BaO_2 , consequently reducing the flow of oxygen to the reaction zone.

D DEPENDENCE OF FLAME VELOCITY ON LAYER DENSITY

Continuous laminae cannot always be used for studying the combustion of layer systems.

(1) There is a limiting value for the layer density for metal powders and possibly for some oxidizer powders, e.g. BaO_2 , so that for $\delta > \delta_{\text{lim}}$ burning does not take place.

(2) There are technical difficulties which in many cases limit the density of a layer. For example in pressing NH_4ClO_4 or KClO_4 into cylindrical perspex tubes the value of δ_{ox} is not greater than 0.90 to 0.95.

When the pressure used in pressing is raised above 1500 to 2000 atm perspex begins to deform. For polystyrene, polyethylene and especially for teflon the limiting values of p_{press} and δ are considerably lower than for perspex.

Special experiments have been made to study the effect of the porosity of the layer on the velocity of the flame along the surface of contact. It was found that the dependence $u(\delta)$ has the same character for volatile and for condensed fusible explosives (see section 2,D); for sufficiently large values of δ , the mass burning rate $u\delta$ decreases slightly with decrease of δ , since the heat release falls with decrease of δ and the heat losses are approximately constant. However at some sufficiently small value of δ , which becomes smaller as the pressure becomes lower, the mass burning rate begins to increase rapidly with decrease in δ , since the hot combustion products begin to penetrate into the pores of the layer*. Such a form of the dependence $u(\delta)$ was obtained for KClO_4 in a cylindrical tube of perspex (Fig.58) and also for aluminium in a coaxial tube of KMnO_4 (Fig.59). With KClO_4 at 40 atm as δ was decreased, the value $u\delta$ after a rapid increase passed through a maximum and began to decrease because of the fall in the total heat release. It is possible that such a decrease in $u\delta$ at very low values of δ may also occur in other cases.

E COMPARISON OF BURNING RATE IN A LAYER SYSTEM AND IN AN ORDINARY DISORDERED MIXTURE

It is interesting to compare (for $d = \text{const}$) the flame velocity along the surface of contact of the layers of fuel and oxidizer u_1 and the burning rate of an ordinary disordered mixture u_{dis} . From theoretical considerations it is obvious^{124,127} that $u_1 > u_{\text{dis}}$, since in disordered systems the flame is retarded by the transmission of burning through a fuel layer.

However experimental verification of $u_1 > u_{\text{dis}}$ is complicated since it is difficult to make a layer system, especially with a large number of layers, for small values of d . The value of u_1 will be reduced with a decrease in the number of layers, down to the limit of two (a layer of oxidizer + a layer of fuel). So far, the experimental values of u_1 have been obtained only

*Consequently for a given value of δ not very close to $\delta = 1$, the dependence of $u(p)$ at a sufficiently high pressure increases sharply. Such an inflection in the curve $u(p)$ was obtained for the layer systems: tungsten (powder, $\delta \sim 0.5$)- KClO_4 (at $p > 50$ atm), tungsten (fraction 140 to 400 μ , $\delta = 0.40$ to 0.45)- KMnO_4 (at $p \sim 100$ atm).

for charges made by pressing oxidizer in powder form into plane or cylindrical channels in the fuel. The density of the layer of oxidizer is thus not very high (usually $\delta \leq 0.6$ to 0.7).

The variation of the density from the maximum can affect u_l and u_{dis} in different ways.

A tentative comparison of u_l and u_{dis} for different values of d for the $KClO_4$ -perspex system is given in Fig. 60. In this case $u_l > u_{dis}$ is valid although the difference is not large. The data were most reliable for a layer system with $d > 4$ to 5 mm and for ordinary mixtures with $d < 0.2$ to 0.5 mm.

Moreover, the value of u_l was obtained for a single layer of oxidizer between two reasonably thick layers of fuel and consequently u_l was reduced; this excess of fuel must also lower u_l since the maximum of the burning rate lies close to $\alpha = 1$ for a $KClO_4$ -perspex system.

In addition, the porosity of the oxidizer layer in the layer system ($1 - \delta = 0.33$ to 0.58) was higher than in the ordinary mixture ($1 - \delta \approx 0.1$); this could raise u_l in comparison with u_{dis} , but not very greatly, since the experiments were carried out at low pressure - 10 atm.

As well as the layer system in which the flame moves along the surface of contact of the stationary (relative to one another) layers of the components, another type of layer system has been studied¹¹³ in which the end of a rod of oxidizer was pressed by a spring against the end of a rod of fuel and thus moved as burning progressed. For rods of perspex and NH_4NO_3 with a certain cross-sectional area of the rods, a mass rate of vaporization of 0.0127 gm/sec was obtained for perspex and of 0.1755 gm/sec for NH_4NO_3 (at 70 atm). This ratio of mass burning rates corresponds to $\alpha \approx 1.44$, i.e. burning takes place with a considerable excess of oxidizer, since NH_4NO_3 vaporizes considerably more easily than perspex.

19 BURNING OF AMMONIUM PERCHLORATE

The burning of ammonium perchlorate (pure or with small additions of fuels and catalysts) has been studied very extensively. It has been suggested that the burning of pure NH_4ClO_4 is one of the elementary processes during the burning of systems of mixtures based on NH_4ClO_4 . Thus the hypothesis has been proposed¹⁴¹ that the burning rate of such systems is simply the burning rate of NH_4ClO_4 taking into account the flow of heat from the diffusion flame.

Such a point of view is useful, but the presence of the fuel which burns in the diffusion flame acts on the burning rate of NH_4ClO_4 in two mutually opposite directions. At first the fuel burning in the diffusion flame must heat up and vaporize. It obtains part of the necessary heat from the $\text{NH}_3 + \text{HClO}_4$ flame and thus retards its burning. However, the fuel then reacts in the kinetic and diffusion flames; part of the heat emitted enters the $\text{NH}_3 + \text{HClO}_4$ flame zone and increases the temperature in this zone. If the percentage of fuel is near to stoichiometric, the second effect predominates and the burning rate of the NH_4ClO_4 -fuel mixture is greatly increased compared with the burning rate of pure NH_4ClO_4 . If the percentage of fuel is very small or conversely is extremely high, or if the fuel is very inert, the first effect predominates and the burning rate of such NH_4ClO_4 -fuel mixtures can be considerably lower than the burning rate of pure NH_4ClO_4 .

Thus the burning mechanism of mixtures based on NH_4ClO_4 can be understood only if the interaction of the components of the mixture is considered.

It is shown below that the burning mechanism of pure NH_4ClO_4 (without fuel) is very different from that of NH_4ClO_4 -fuel mixtures.

The burning of pure NH_4ClO_4 is characterized by sharply defined limits and it is therefore very sensitive to changes in the conditions of burning. For the burning of NH_4ClO_4 specimens in an atmosphere of compressed nitrogen there are a lower p_L and upper limit p_U with respect to pressure so that burning is stable only in the interval $p_L < p < p_U$. The value of p_L and p_U (and the very existence of the upper limit) depend on the character of the charge casing, on the diameter of the charge, on the relative density of the charge and on the NH_4ClO_4 particle size, etc.

The burning of NH_4ClO_4 is much more sensitive to an increase in the initial temperature than the burning of mixtures of NH_4ClO_4 which are not too far from stoichiometric; the temperature coefficient β is in the first case $(5.6 \text{ to } 6.0) \cdot 10^{-3} \text{ deg}^{-1}$ (Ref.47) and in the second case $(1 \text{ to } 2) \cdot 10^{-3} \text{ deg}^{-1}$.

In the same way pure NH_4ClO_4 is much more sensitive to the effect of additives than compositions based on NH_4ClO_4 (see section 17).

The dependence of the burning rate of NH_4ClO_4 on the relative density δ also testifies to the limited character of its burning. With decrease in δ not only the mass rate of burning but the linear rate of burning decreases, whereas for secondary explosives and mixtures the linear burning rate generally increases with decrease of δ .

Finally when small additions of fuel are made to NH_4ClO_4 , the burning rate can not only not rise but may even decrease considerably as far as the point where burning is extinguished, since the diffusion flame is feeble and does not compensate for the heat lost in heating and vaporizing the fuel.

The limited character of the burning of pure NH_4ClO_4 is essentially connected with its low combustion temperature (the calculated temperature is 1380°K at 1 atm abs)¹⁵⁰, whereas the combustion temperature of compositions based on NH_4ClO_4 is usually not less than 2300 to 2700°K at 1 atm abs (Ref.126).

A LOWER AND UPPER PRESSURE LIMITS OF BURNING

Data on the lower limit of burning are given in Refs.120, 173, 188, 189, 251, etc. It was found that the value of p_L decreases under the following conditions:

(1) With increase in the particle size of NH_4ClO_4 (Refs.102, 189, 251). Thus for example the results obtained²⁵¹ at 20°C were:

$d_{\text{NH}_4\text{ClO}_4}, \mu$	< 50	50 to 63	63 to 100	160 to 250	250 to 316
p_L, atm	110	70	70	40	23

Data from Ref.189 are given in Fig.61.

(2) With increase in the initial temperature of the charge (Refs.47, 120, 180, 251). Thus for example the results obtained²⁵¹ for $d_{\text{NH}_4\text{ClO}_4} < 50 \mu$ were:

$T_0, ^\circ\text{C}$	20	60	100	120
p_L, atm	110	50	36	30

(3) With the addition of catalysts (Refs.47, 173, 190, etc).

(4) With increase in the diameter (ϕ) of the charge. Thus $p_L = 50 \text{ atm}$ was obtained¹²¹ for $\phi = 5 \text{ mm}$ and $p_L = 30 \text{ atm}$ for $\phi = 7 \text{ mm}$.

(5) With increase in the relative density $\delta = \rho/\rho_{\text{max}}$ of the charge. Thus $p_L \approx 80 \text{ atm}$ was obtained¹⁷³ for $\delta \approx 0.65$ and $p_L \approx 60 \text{ atm}$ for $\delta \approx 1$.

The value of p_L can be greatly reduced when a fuel casing is used (see below).

Additionally, the value of p_L depends on the character of the igniter. Thus when a glowing filament igniter is used $p_L \approx 45$ atm and for an igniter composition $p_L \approx 22$ atm¹⁸⁸.

The value of the upper limit p_U (and the existence of an upper limit) is now considered. The presence of catalytic additives¹²⁰ and also the character of the casing^{152,188} affects the value of p_U . Thus it was discovered¹⁸⁸ that for a charge in an asbestos tube an upper limit is not observed, at least for $p \leq 300$ atm, whereas for a charge without a casing $p_U \approx 250$ atm. The burning of a charge without a casing was extinguished¹⁵² at $p > 280$ atm; on the other hand the burning of a charge in an asbestos casing was stable up to at least 1600 atm.

The existence of pressure limits for the burning of NH_4ClO_4 is undoubtedly associated with heat losses from the combustion zone of $\text{NH}_3 + \text{HClO}_4$. The lower limit evidently depends to a considerable extent on the intensity of combustion of NH_4ClO_4 , which increases with increase in pressure up to a limiting value. Thus for example the composition of the combustion products of NH_4ClO_4 was measured¹⁸⁸ and it was shown that at 1 atm abs (evidently combustion was assisted by an auxiliary supply of heat from a projector) the actual composition of the combustion products diverges considerably from those expected from $\text{NH}_4\text{ClO}_4 \rightarrow 0.5\text{N}_2 + \text{HCl} + 1.5\text{H}_2\text{O} + 1.25\text{O}_2$ since the combustion products contain a large quantity of oxides of nitrogen. However with increase in pressure the oxides of nitrogen decrease and the oxygen increases correspondingly (Table 54).

TABLE 54

Influence of pressure on the composition of the combustion products of NH_4ClO_4

Pressure, atm	No. of moles of products per mole NH_4ClO_4				Ref.
	NO_2	N_2O	N_2	O_2	
1	0.55	0.10	0.11	0.65	188
35	0.31	0.11	-	0.75	
70	0.23	0.12	-	0.80	
140	0.23	0.05	-	0.80	
1	0.54 (mole NO)	0.145	0.085	0.73	103
73.5	0.013 (mole NO)	0.11	-	0.78	

The loss of energy by radiation from the $\text{NH}_3 + \text{HClO}_4$ flame and from the NH_4ClO_4 surface to the surrounding volume can also be considerable as a result of the limited character of the burning of NH_4ClO_4 .

The upper limit is possibly connected with the convection losses from the flame zone to the surrounding gas since these losses increase with increase in pressure.

An increase in the temperature in the $\text{NH}_3 + \text{HClO}_4$ flame zone can extend the limits of burning considerably and thus the upper limit of burning in general cannot be observed for the whole of the pressure range studied.

Such a temperature increase in the flame zone can be achieved as follows:

- (1) by an increase in the initial temperature of the charge,
- (2) by a supplementary flow of radiative heat, incident on the surface of the charge from an outside source,
- (3) by the addition of catalysts which reduce the width of the combustion zone and hence lower the heat losses from the flame zone. In those cases where the intensity of combustion is low, catalytic additives can increase it,
- (4) by additions of fuel* (in not too small amounts) or by the use of a fuel casing,
- (5) by decreasing the heat losses from the flame zone due to the use of an inert casing with low thermal conductivity.

Many experiments have been carried out to elucidate the particular problem of the minimum preheating required to enable NH_4ClO_4 to burn at 1 atm abs. Thus it was found⁴⁷ that pure NH_4ClO_4 ($\delta \approx 0.54$) at 1 atm abs burns at $T_0 \geq 200^\circ\text{C}$. If the value $c \approx 0.26 \text{ cal gm}^{-1} \text{ deg}^{-1}$ is taken for the specific heat of NH_4ClO_4 , this preheating amounts to 52 cal/gm. The minimum preheating due to an increase in T_0 is estimated as 64 cal/gm and that due to an addition of volatile fuel as not less than 107 cal/gm (i.e. approximately 1.7 times greater)¹⁰³. This discrepancy is to be expected since only the part

*Addition of fuels leads to the appearance of the diffusion flame and a considerable flow of heat to the surface of the charge. However a definite quantity of heat is also required to heat and vaporize the fuel. Therefore the burning rate can fall for a small percentage of added fuel, increase in the fuel percentage even resulting in complete extinction at pressures at which pure NH_4ClO_4 burns steadily. However, for higher fuel percentages the temperature in the $\text{NH}_3 + \text{HClO}_4$ zone rises, the stability of burning improves and the burning rate also begins to rise rapidly.

of the heat emitted in the diffusion flame reaches the $\text{NH}_3 + \text{HClO}_4$ reaction zone. Moreover the flow of heat from the diffusion flame is partially expended in the preheating and vaporization of the added fuel and only the remaining part of the heat is used to preheat the NH_4ClO_4 . The minimum flame temperature of NH_4ClO_4 for which burning is stable at 1 atm abs is $\approx 930^\circ\text{C}$ in the case where volatile fuels are added, but in the case of an addition of carbon the final temperature of the flame must be not less than 1600°C , since carbon reacts slowly and the portion of heat reaching the surface of the charge is small.

The minimum flow of heat using radiation from projector equipment for which NH_4ClO_4 could burn at 1 atm abs was found¹⁸⁸ to be $10 k_{\text{abs}} \text{ cal. cm}^{-2} \text{ sec}^{-1}$ where k_{abs} the coefficient of absorption is approximately equal to $1 - 0.63 = 0.37$, assuming that the transmission coefficient is close to zero. The burning rate was $\approx 0.2 \text{ mm/sec}$. Taking $\delta \approx 1$ ($\rho \approx 1.95 \text{ gm/cm}^3$) the minimum preheat required was $\frac{10 \times 0.37}{1.95 \times 0.02} = 95 \text{ cal/gm}$.

Catalytic additives and also a fuel casing can extend the limits of burning very considerably, though quantitative assessments of the temperature rise in the flame zone have not been made.

A considerable number of catalytic additives has been described which ensure the stable burning of NH_4ClO_4 at 1 atm abs and room temperature, for example, CuO , Cu_2Cl_2 , MnO_2 , MnCO_3 (see Ref.190, $\delta \approx 0.6$ to 0.65); Cu_2O (Ref.173, $\delta \approx 0.84$; Ref.190, $\delta \approx 0.6$ to 0.65); copper chromite (Ref.47, $\delta \approx 0.4$), etc.

The disappearance of p_{fl} was observed¹²⁰ (at least in the range up to $p = 340 \text{ atm}$) for the addition of (3%) copper chromite, CuO , Cr_2O_3 , Fe_2O_3 , MnO_2 , etc, whereas without any additive $p_{\text{fl}} \approx 280 \text{ atm}$.

A fuel casing improves the stability of burning very considerably. Thus NH_4ClO_4 burns steadily in a perspex casing or with a sufficiently thick film of lacquer at least over the range from several atmospheres¹⁷³ up to $p \approx 1000 \text{ atm}$ ¹²¹.

B BURNING RATE AT VARIOUS PRESSURES

Owing to the limited character of the burning of NH_4ClO_4 the absolute value of the burning rate at various pressures and even the form of the $u(p)$ curve depend considerably on the conditions under which the experiments are

carried out even within the limits of a single work and especially when referring to different works*.

The form of the curve $u(p)$ is now considered. Despite the great diversity of the data, three portions of the curve $u(p)$ can be quite clearly distinguished.

(1) At 'low' pressures from p_L to pressures of 70 to 200 atm the burning rate rises monotonically with increase in pressure. The dependence $u(p)$ at low pressures was found^{120,121,173,188,189} to be close to one of direct proportion ($\nu \approx 0.8$ to 1.0; see Table 55 and also Fig.62 at $p \leq 150$ atm). However for uncased charges¹⁴¹ of NH_4ClO_4 (5×5 mm) and also for charges of NH_4ClO_4 smeared with a fluorinated grease¹²¹ the value of ν (over the ranges 70 to 210 and 50 to 200 atm respectively) was only 0.34 to 0.58 (Table 55).

(2) At 'medium' pressures from 70-200 to 300-500 atm the burning rate either continues to increase with rise in pressure, although much more slowly than at 'low' pressures (see Table 55), or flattens out into a plateau, or falls with increase in pressure over a certain pressure range and then begins to rise (Fig.62 at 150 to 200 atm), or, finally, with increase in pressure decreases to the point where burning is extinguished (Fig.64).

(3) At 'high' pressures (higher than 300 to 500 atm) a sharp increase in the dependence $u(p)$ is observed^{121,152} (see Table 55 and Figs.62, 63).

The 'low' pressure region will be examined in greater detail. Many, but not all, authors find the dependence $u(p)$ in this region to be close to the dependence $u = bp$, which is characteristic of volatile homogeneous explosives. This is to be expected, since NH_4ClO_4 is essentially a weak homogeneous explosive.

However, owing to the limited character of the burning of NH_4ClO_4 , the analogy with volatile homogeneous explosives is restricted and easily infringed.

In particular the burning rate of NH_4ClO_4 can depend^{120,189,251} to a great extent on the particle size of the powder from which the charge is pressed whereas for secondary explosives for $\delta \approx 1$ the particle size of the original powder has practically no influence on the burning rate. Data on the dependence $u(d_{\text{NH}_4\text{ClO}_4})$ are shown in Figs.64 and 65. In Fig.65 the

*The experiments in Refs.120, 121, 141, 173, 188, 189 were carried out in a constant pressure bomb and in Ref.152 in a manometric bomb.

TABLE 55

Value of exponent ν in equations $u = bp^\nu$, or $m = b'p^\nu$,
for NH_4ClO_4 with various casings

d_{ex}, μ	Casing material	Diameter of charge, mm	ν			Ref.
			'Low' pressures	'Medium' pressures	'High' pressures	
~15 100-140 ~15 100-140 ~15 ~15 320-410	Perspex	7	0.88 (10-150)	at 150-200 atm $\nu < 0$	~2.0 (360-950)	121
	Polyvinyl chloride lacquer	7 15		~0 (100-250)	~1.6 (350-1000)	
	Fluorinated grease	7	0.53 (50-200)	0.14 (200-500)	~1.3 (500-1000)	
	Cement + glass	10	0.93 (40-100)			173
	Cement + glass	10	0.82 (60-100)			
	Perspex $\delta_{\text{NH}_4\text{ClO}_4} \geq 0.95$	6	0.91 (10-100)			
	Perspex $\delta_{\text{NH}_4\text{ClO}_4} = 0.67$ to 0.74	6	0.90-0.92 (5-100)			188
	Perspex $\delta_{\text{NH}_4\text{ClO}_4} \geq 0.94$	6	~0.90 (40-100)			
	Asbestos	4 x 4	1.06 (30-50) 0.69 (50-100)	0.36 (100-300)		
	Asbestos	16		0.25 (70-350)	1.75 (350-1500)	152
53-66	Without casing	5 x 5	0.585 (70-210)			141
66-76	" "	5 x 5	0.585 (70-210)			
76-104	" "	5 x 5	0.57 (70-210)			
~15 recrystallized	" "	5 x 5	~0.5 (140-210)			
~15 Specimen 'A'	" "	5 x 5	0.34 (70-210)			
~15 Specimen 'B'	" "	5 x 5	0.57 (140-210)			

Note: The figures in brackets () denote the pressure range in atm.

burning rate at 100 atm changes from ≈ 10 mm/sec (for the fraction 300 to 3000 μ) to ≈ 4.5 mm/sec (for the fraction 5 to 250 μ), i.e. by a factor of 2.2.

It can also be seen from Fig. 64 and 65 that there is no monotonic relationship between the particle size of NH_4ClO_4 and its burning rate, although very wide fractions of NH_4ClO_4 evidently have a higher burning rate.

However this dependence of u on the particle size of NH_4ClO_4 has not always been observed. Thus the data in Ref. 141 (at 105 atm) and in Ref. 173 (at 100 atm) indicate that the particle size of NH_4ClO_4 only slightly affects the burning rate (Table 56).

The significance of the effect of particle size on the burning rate of charges of NH_4ClO_4 compressed to a high density is not yet clear.

TABLE 56

Effect of particle size of NH_4ClO_4 powder from which charges
are pressed ($\delta \approx 1$) on the burning rate

Fraction NH_4ClO_4 , μ	u , mm/sec	Coating material	Diameter of charge, mm	Ref.
~ 15	12	Cement + glass	10	173
< 100	9.9	Cement + glass	10	
100-140	10	Cement + glass	10	
~ 15	11.4	Perspex	6	
320-410	12	Perspex	6	
53-66	8.9	Uncoated	5×5	141
66-76	8.6	Uncoated	5×5	
76-104	7.9	Uncoated	5×5	

Many authors have found that a hot charge of NH_4ClO_4 does not have a plane surface. It is possible that the surface area of a hot charge depends on the particle size of the powder from which the charge is pressed, which can affect the burning rate.

Impurities on the surface of the crystals, which can either retard or accelerate the burning rate, can play a definite role. The percentage of the impurities can change during the process of preparing different fractions;

it can increase during the grinding of NH_4ClO_4 in mills and can decrease during recrystallization.

In many cases it is interesting to compare the burning rate of pure NH_4ClO_4 with that of compositions based on it. From what has been said above it is clear that the burning rate of pure NH_4ClO_4 must be determined for that batch and that fraction which is used in the composition.

Nevertheless certain mean values of the burning rate which are readily available can be used for tentative comparisons:

p, atm	40	60	80	100
\bar{u} , mm/sec	4	6	8	10

The significance of the unusual form of the curve $u(p)$ for NH_4ClO_4 at 'medium' and 'high' pressures is uncertain in many respects. For medium pressures very convincing arguments are put forward on the role of convective heat losses^{152,188}. As convective heat losses become more significant, the dependence $u(p)$ becomes increasingly less down to the point where burning is completely extinguished. When a casing of fuel is used¹²¹ burning becomes more stable compared with the burning of a charge without a casing, but in this case the dependence $u(p)$ decreases sharply up to the point where there is a fall in the burning rate with increase in pressure in a certain pressure range.

The region of 'high' pressures, which was investigated only in Refs. 121 and 152, is even less clearly understood. The sharp increase in the dependence $u(p)$ close to 350 atm (the exponent ν in the equation $u = bp^\nu$ was 0.251 at 70 to 350 atm and increased to $\nu \approx 1.75$ at 350 to 1500 atm) was related¹⁵² to the cracking of the charge of NH_4ClO_4 due to the thermal stresses at the high burning rate and also to the rapid increase in pressure in the manometric bomb in which the experiments were carried out.

However a sharp increase in the dependence $u(p)$ at $p > 300$ to 500 atm was observed in a constant pressure bomb by A.P. Glazkova¹²¹. Hence the rise of pressure in the volume was not a necessary condition for an increase in the exponent ν . Apart from this it was shown that the exponent ν depends considerably on the nature of the casing (for charges in casings of perspex $\nu_{p=360 \text{ to } 950 \text{ atm}} \approx 2.0$; for charges coated with a layer of fluorinated grease $\nu_{p=500 \text{ to } 1000 \text{ atm}} \approx 1.3$; Table 55). It is also most significant that for

NH_4ClO_4 catalysed by 5% $\text{K}_2\text{Cr}_2\text{O}_7$ (according to the data of A.P. Glazkova²²⁷) the curve $u(p)$ at $p \leq 1000$ atm is quite 'smooth' ($\nu = \text{const} \approx 0.6$) and at all points is above the curve $u(p)$ for pure NH_4ClO_4 . Hence it follows that a sharp increase in the dependence $u(p)$ for pure NH_4ClO_4 at $p > 300$ to 500 atm is not necessarily related to the break down of laminar burning. Possibly the increase in the dependence $u(p)$ at 'high' pressures, and also the decrease in the dependence $u(p)$ at 'medium' pressures, is a result of the limited character of the burning of NH_4ClO_4 and reflects the temperature changes in the reaction zone with rise in pressure. The introduction of a catalyst improves the ratio of the heat gain to the heat losses and thus the curve $u(p)$ assumes the normal form.

In the previous section it was observed that a rise of temperature in the burning zone of NH_4ClO_4 due to an increase in the initial temperature, to catalytic additives, to fuel* or to the use of a fuel casing can considerably extend the limits of burning.

A temperature rise in the burning zone must also result in an increase in the burning rate. This has been investigated most thoroughly at 'low' (≤ 70 to 150 atm) pressures.

The dependence of the burning rate of NH_4ClO_4 (pure and with the addition of 3% copper chromite) on the initial temperature has been studied⁴⁷ for the relative densities $\delta \approx 0.4, 0.56$ and 0.95 and pressures 1, 20, 40 and 50 atm. In all cases, within the limits of accuracy of the experiment, the value of the temperature coefficient $\beta = d \ln u / dT_0$ was in the same range⁶ $\beta = (5.6 \text{ to } 6.0) \cdot 10^{-3} \text{ deg}^{-1}$ (Fig.66). The value of β for NH_4ClO_4 is very much higher than for mixtures of NH_4ClO_4 with fuels (for α not too far from $\alpha = 1$), where $\beta \approx (1 \text{ to } 2) \cdot 10^{-3} \text{ deg}^{-1}$ and than for gas mixtures

*See footnote p.162.

⁶Such a constant value of β is surprising to a certain extent; β might be expected to decrease with increase in pressure and the addition of a catalyst, since in this case the intensity of combustion increases (see above). However it was shown in section 2, A, C that the temperature coefficient depends on the effective temperature in the combustion zone. In the case of NH_4ClO_4 without fuel, the effective temperature can change only between narrow limits, since even for an equilibrium product composition the combustion temperature is very low (1380°K at 1 atm abs (Ref.150)) and therefore a relatively small decrease in the intensity of combustion results in the extinction of combustion, and it has been deduced¹⁰³ that burning at 1 atm abs is stable only at $T_c \geq 1200^\circ\text{K}$. Consequently the value of β for NH_4ClO_4 without fuel can change only within relatively narrow limits.

($\beta = 2 \cdot 10^{-3} \text{ deg}^{-1}$), but is close to the value for liquid nitroesters (see section 2,C) where burning takes place in two stages, and the burning rate is determined by the first low-temperature stage.

Thus a rise in the initial temperature and also the addition of catalysts (see section 17) have a marked effect both on the limits of burning and the burning rate of NH_4ClO_4 . However a different state of affairs is involved when fuel is added or a fuel casing is used.

Small additions of fuel can in some cases reduce the burning rate of NH_4ClO_4 even to the point of extinction of burning - in which case the limits of burning with respect to pressure also become narrower. As an example the experiments with additions of bitumen and urotropine¹⁷³ (Tables 57 and 58 and Fig.67) can be quoted.

The cause of such a reduction in the burning rate was examined at the beginning of section 19. It is observed that for small additions of urotropine (Table 58) the most significant reduction in the burning rate occurs at high pressures (100 atm), but at low pressures (5 to 10 atm) the burning rate generally does not decrease. This result is to be expected since, as the pressure increases, the width of the zone of influence decreases

TABLE 57

Burning rate of lean NH_4ClO_4 + bitumen mixtures ($\delta \sim 1$)
with an inert casing (phosphate cement-glass)¹⁷³

Fraction NH_4ClO_4 , μ	p, atm	u (mm/sec) for bitumen content by wt %				
		Without bitumen	2.2	2.7	3.6	5.3
~15	10	0	0	0	3.0	5.5
	40	5.2	0	0	5.2	10.1
	60	7.4	0	0		
	80	10.0	0	0		
	100	12.0	0	7.5	11.7	21.9
100-140	10	0		0		3.6
	40			0		7.1
	60	6.6		5.6		
	80			7.1		
	100	10.0		7.8		13.0
	120			9.6		

Note: Zero denotes that the mixture does not burn at the given pressure.

TABLE 58

Burning rate of mixtures of NH_4ClO_4 ($\approx 15 \mu$) with urotropine
 (< 30 to 40μ) in perspex casing¹⁷³

$\delta \approx 0.95$ to 0.98 , diameter of charge 6 mm

p, atm	u (mm/sec) for content of urotropine by wt %				p, atm	u (mm/sec) for content of urotropine by wt %			
	0	2	4	14.2 ($\alpha = 1$)		0	2	4	14.2 ($\alpha = 1$)
5	0.68	0.98	1.40	3.9	40	4.9	3.8	4.2	16.6
10	1.51	1.42	1.77	6.0	100	11.4	8.4	6.5	28.3

(see section 10,B) and the ratio of the heat losses in preheating and vaporizing the particles of fuel to the heat conducted from the diffusion flame zone becomes less favourable*. Data are given¹⁰³ on the narrowing of the limits of burning and the reduction of the burning rate for small additions of non-volatile fuels. Here the decisive role is played by radiation losses and in this connection the effect of the fuel colour is to be emphasized; a given percentage of black particles can suppress burning, but white particles do not interfere with burning.

A fuel casing greatly reduces the lower pressure limit and can, though not very markedly, have an effect on the burning rate at 'low' pressures (see, for example, Table 56). In this case the heat transfer from the diffusion flame at the edges of the charge does not raise the burning rate of NH_4ClO_4 to any significant extent and only compensates for the heat lost in vaporizing the fuel, but at the same time by acting as a pilot flame it does not allow the temperature of the $\text{NH}_3 + \text{HClO}_4$ flame to fall below a certain level.

*For a high fuel percentage the burning rate is increased in comparison with the burning rate of pure NH_4ClO_4 over the whole pressure range investigated, but this increase is greater at low pressures than at high pressures; thus the ratio of the burning rate of the mixture NH_4ClO_4 with 14.2% urotropine to the burning rate of pure NH_4ClO_4 is 5.75 at 5 atm and only 2.5 at 100 atm.

C DEPENDENCE OF BURNING RATE ON DENSITY

In section 2,D it was shown that the character of the curve $u(\delta)$ where $\delta = \rho/\rho_{\max}$ is the relative density of the charge can vary with the conditions under which the reaction takes place and with the extent of heat losses.

If the reaction takes place in the gas phase or in a melt and there are no heat losses then $u\delta = \text{const} \neq f(\delta)$. Under the same conditions but in the presence of heat losses, the product $u\delta$ decreases as δ decreases (since the heat release decreases in proportion to the decrease in δ , but the heat losses, to a first approximation, do not depend on δ and are determined by the flame temperature and the temperature of the surrounding medium, and by the nature of the casing, etc). However for secondary explosives (see section 2,D) the linear burning rate u usually increases with δ in the region of laminar burning, and especially in the region of convective burning where a sharp increase in u and $u\delta$ is observed as δ is reduced.

For NH_4ClO_4 with an inert casing, the linear burning rate u and even more so the product $u\delta$ decrease with decrease in δ (Table 59). Moreover the stability of burning of NH_4ClO_4 for $\delta = 0.75$ and 0.65 was low; in some experiments burning was intermittent, the charge did not burn completely and the scatter of the results was wide (the figures given in Table 59 are mean values taken from a large number of experiments).

TABLE 59

Dependence $u(\delta)$ for NH_4ClO_4 (particle size 100 to 140 μ)
in an inert casing¹⁷³

For $\delta \approx 1$ phosphate cement-glass; for $\delta = 0.75$ and 0.65 , glass; diameter of charge 10 mm

p, atm	u, mm/sec			u δ		
	$\delta = 1$	$\delta = 0.75$	$\delta = 0.65$	$\delta = 1$	$\delta = 0.75$	$\delta = 0.65$
60	6.6	4.6	-	6.6	3.4	-
100	10.0	6.7	6.5	10.6	5.0	4.2

The burning of NH_4ClO_4 in perspex casings has a less limited character owing to the diffusion flame at the edges of the charge. In this case the linear burning rate does not decrease with decrease in δ but increases

(Table 60). Although the product $u\delta$ decreases with increase of δ , the decrease is considerably less than for NH_4ClO_4 with an inert casing. As regards the stability of burning, NH_4ClO_4 in perspex casings for $\delta \geq 0.7$ burns completely at a pressure of a few atmospheres, whereas NH_4ClO_4 with an inert casing, or uncased, does not burn below 20 to 40 atm. The scatter of results for NH_4ClO_4 in a perspex casing is considerably less than for NH_4ClO_4 with an inert casing.

TABLE 60
Dependence $u(\delta)$ for NH_4ClO_4 in a perspex casing
(diameter of charge 6 mm)¹⁷³

Particle size NH_4ClO_4 , μ	p, atm	u, mm/sec		$u\delta$	
		$\delta = 0.96$	$\delta = 0.72$	$\delta = 0.96$	$\delta = 0.72$
15	5	0.68	1.0	0.65	0.72
	10	1.5	1.6	1.44	1.15
	40	4.9	5.9	4.7	4.25
	100	11.4	12.6	11.0	9.1
320 to 410	5	0.63	0.78	0.6	0.56
	10	1.04	1.55	1.0	1.1
	40	5.4	Sudden change in burning rate	5.2	-
	100	12.0	"	11.5	-

If a sufficiently efficacious catalytic additive is mixed with NH_4ClO_4 , the width of the combustion zone is decreased and consequently the heat losses are reduced. In a number of cases the intensity of combustion increases. Therefore the burning of catalyzed NH_4ClO_4 with an inert casing may be completely stable at low pressures, but the product $u\delta$ remains constant as δ is decreased.

Thus the following results were obtained for NH_4ClO_4 ($\approx 15 \mu$) with the addition of 2% Cu_2O (p = 1 atm abs, glass casing, $\phi = 10 \text{ mm}$)¹⁷³:

δ	0.84	0.62	0.59	0.54	0.38
$u\delta$, mm/sec	0.92	0.98	0.94	0.94	0.95

Finally, experiments carried out with pure NH_4ClO_4 with an inert coating, but at an elevated initial temperature showed that the product $u\delta$ decreases with decrease in δ to lesser extent as T_0 is increased (compare Tables 59 and 61).

TABLE 61

Dependence $u(\delta)$ for pure NH_4ClO_4 with an inert casing at an elevated initial temperature (pressure 20 atm)¹⁷³

δ	$u\delta$, mm/sec	T_0 , °C	δ	$u\delta$, mm/sec	T_0 , °C
0.98	3.3	100	0.98	4.4	150
0.75	2.9	100	0.62	4.2	150
0.62	2.5	100			

At 150°C the mass burning rate is almost independent of δ .

The results of experiments on the dependence $u(\delta)$ are in agreement with the idea that the burning of NH_4ClO_4 takes place in the gas phase and is very sensitive to heat losses. If the leading reaction took place in the condensed phase, then an increase in the initial temperature or an addition of catalyst could raise the absolute value of the burning rate, but it could not give $u\delta = \text{const.}$

* * *

In concluding section 19 it is observed that the absolute value of the burning rate of NH_4ClO_4 is reasonably high despite the low combustion temperature and the high sensitivity to heat losses. At 40 to 100 atm it lies within the same limits as the burning rate of many explosives (such as PETN, tetryl, see Table 13) and considerably exceeds the burning rate of such explosives as dynamite, picric acid and trotyl (TNT), although their combustion temperatures are 1.5 to 2.5 times higher than for NH_4ClO_4 . However, the burning of many explosives containing NO_2 groups takes place in two stages and the burning rate is determined mainly by the first, the low temperature stage. In section 2,A it was observed that the burning rate of volatile explosives was evidently close to the (mass) burning rate of gas mixtures based on NO_2 . On the other hand the burning rate of NH_4ClO_4 is small (or very small) in comparison with the (mass) burning rate of gas mixtures with

oxygen (see Table 4) and evidently with HClO_4 (see the beginning of section 10), although reliable comparisons cannot be made since the experimental data are limited. The burning rate of NH_4ClO_4 , even without a catalyst, is considerable higher (4 to 5 times) than the burning rate of NH_4NO_3 (with catalytic additives).

Finally, if the burning rate of NH_4ClO_4 is compared with the burning rate of mixtures of NH_4ClO_4 with fuels, then (see the beginning of section 19), depending on the percentage of fuel and its properties, various types of relationships between these burning rates are possible. Very small additions of fuels can lower the burning rate of NH_4ClO_4 considerably. Mixtures near stoichiometric can have a burning rate much greater (2 to 4 times) than the burning rate of NH_4ClO_4 , although the burning rate of a mixture depends largely on the particle size of the components, on the reactivity of the fuel and its heat of combustion and on the heat lost in preheating the fuel and - in the case of volatile fuels - in effecting vaporization, etc. On the other hand the burning rate of mixtures with a large excess of fuel can be considerably lower than the burning rate of pure NH_4ClO_4 .

20 BURNING RATE OF BLACK POWDER

Black powder consists of a mixture of KNO_3 , wood charcoal and sulphur. The proportions of the components can vary to some extent; usually the composition is 75% KNO_3 , 15% wood charcoal and 10% sulphur (the powders Mark DRP-1 and Mark DRP-3 have compositions close to this).

Black (or smoke-forming) powder is the oldest mixed system, having been employed both as gunpowder and as an explosive for many centuries. In recent times, the use of black powder has become extremely limited. It is used (see Ref.219) in time fuzes, in igniters, in the pyrophoric (Bickford) fuze, in sporting guns, etc.

The study of black powder, apart from its immediate interest, is useful for understanding the mechanisms characteristic of systems in which carbon particles are present in the combustion zone.

Thus the theoretical work^{62,225,226} carried out specially for black powders is of great interest, since examination of the experimental data allows theory to be compared with experiment.

A DEPENDENCE ON PRESSURE

It was already observed in early work (the results of which are given in Ref.219) that the dependence $u(p)$ for black powder was marked at low

pressures, but became weaker with increase of pressure. Thus, the data of Saint-Robert, at pressures below one atmosphere gave a value of the exponent ν in the equation $u = bp^\nu$ close to $\nu = 0.7$. At high pressures, according to Vielle's data, $\nu = 0.3$ to 0.5 .

Baum and Levkovich²³⁰ obtained the value $\nu = 0.505$ for smoke-forming powder at 1 atm abs, but at high pressures (in a manometric bomb) $\nu = 0.17$.

Shapirc²²⁰ evaluated the data of several authors and obtained the following results:

p, atm	0.4	1.0	2.0	3.0	500
ν	1.00	0.63	0.49	0.40	0.33

According to Andreev²²¹, for a Bickford fuze, $\nu = 0.5$ at $p < 2$ to 2.5 atm, and above this pressure, $\nu = 0.24$.

The decrease in the dependence $u(p)$ for black powder with increase of pressure has been observed more recently^{42,44,163}. Thus the following values for the coefficients b and ν in the equation u (mm/sec) = bp^ν (atm) were obtained:

Ref.	163	42	44	44
p, atm	0.25 to 5	10 to 1000	400 to 2000	1500 to 4500
ν	0.50	0.216	0.25	~0.0
b	8.8	2.3*	8.0	~60

The experiments were carried out in a constant pressure bomb^{42,163} and in a variable pressure bomb⁴⁴. Powder Mark DRP-1 was investigated in Ref.42 and Mark DRP-3 in Ref.44. The experimental values obtained^{42,44,163} are plotted on $\log u$, $\log p$ coordinates in Fig.68 and this shows clearly the decrease in the dependence $u(p)$ with increase of pressure. It is possible to represent approximately the $\log u = f(\log p)$ curve as four separate straight lines. The corresponding values $c^\circ \nu$ are:

*This value is for b' in the equation $m(\text{gm cm}^{-2} \text{ sec}^{-1}) = b'p^\nu$ (atm).

p, atm	0.1 to 0.25	0.25 to 3	1 to 1000	1000 to 4000
ν	1.08	0.56	0.226	0.118

In spite of the considerable scatter of the experimental points, the most reliable data are certainly those for the range 1 to 1000 atm, since the straight line with $\nu = \text{constant}$ is obtained from the results of three independent works.

Data are given¹⁶³ on the dependence of the exponent ν in the equation $u = bp^\nu$ on the proportions of the components in a KNO_3 -wood charcoal mixture (black powder without sulphur):

% KNO_3 /% charcoal	92/8	85/15	76/24	68/32
α^*	2.13	1.05	0.59	0.39
ν	0.57	0.50	0.28	0.30
Pressure, atm	12.5 to 100	5 to 125	1 to 100	1 to 100

Thus the dependence $u(p)$ for KNO_3 -wood charcoal mixtures is reduced with increase of excess fuel, which is similar to the results obtained for sufficient excess fuel in KClO_4 -graphite and KClO_4 -tungsten mixtures, see section 14.

B DEPENDENCE ON INITIAL TEMPERATURE

At moderate initial temperatures and pressures not far above atmospheric the dependence $u(T_0)$ for black powder is very slight:

Ref.	159	159**	224	224
p, atm	1	-	1	10
T, °C	0 to 100	-30 to +44	20 to 115	20 to 125
$\beta \cdot 10^3, \text{deg}^{-1}$	1.5 ± 0.4	0.65	0.50	~ 1.0

However, at very high values of T_0 the dependence $u(T_0)$ can increase substantially²²⁴ (for example, at 1 atm abs, $\beta_{20-115^\circ\text{C}} = 0.50 \cdot 10^{-3} \text{ deg}^{-1}$ and $\beta_{115-250^\circ\text{C}} \approx 1.9 \cdot 10^{-3} \text{ deg}^{-1}$; at 10 atm, $\beta_{75-225^\circ\text{C}} \approx 3 \cdot 10^{-3} \text{ deg}^{-1}$).

*For evaluating α the wood charcoal composition was taken as $\text{C}_6\text{H}_2\text{O}$.

**Data of F.A. Baum.

The dependence $u(T_0)$ for powder without sulphur, consisting of 85% KNO_3 and 15% wood charcoal, was also studied²²⁴. The value of β for 'sulphurless' powder at 1 atm abs and moderate initial temperatures is substantially higher ($\beta_{20-115^\circ\text{C}} \approx 4 \cdot 10^{-3} \text{ deg}^{-1}$) than for ordinary powder ($\approx 0.5 \cdot 10^{-3} \text{ deg}^{-1}$). At high values of T_0 the value of β for 'sulphurless' powder (KNO_3 -wood charcoal) reaches $7 \cdot 10^{-3} \text{ deg}^{-1}$. However it must be stressed that the data on the dependence $u(T_0)$ at high values of T_0 have as yet been obtained from only one source²²⁴, and therefore it is not possible to appraise their reliability.

C DEPENDENCE ON COMPOSITION

Experiments were carried out¹⁶³ with black powder of the usual composition (75% KNO_3 , 15% wood charcoal, 10% sulphur) which has a value of α of 0.7 and with binary KNO_3 -wood charcoal mixtures with the proportions 92:8, 85:15, 76:24 and 68:32, the corresponding values of α being 2.1, 1.05, 0.6 and 0.4.

From the aspect of heat of combustion, sulphur is far less effective than carbon, since the heat of combustion of a stoichiometric S- KNO_3 mixture is merely $\approx 100 \text{ cal/gm}$ and that of a stoichiometric C- KNO_3 mixture is $\approx 370 \text{ cal/gm}$. Nevertheless it has been shown that the burning rate of ordinary black powder (with 10% sulphur) in the pressure range studied (1 to 125 atm) is substantially greater (see straight line 1 of Fig.69) than the burning rate of binary KNO_3 -wood charcoal mixtures with the proportions 85:15 ($\alpha \approx 1.05$, see straight line 3 of Fig.69) or 76:24 ($\alpha \approx 0.6$, see straight line 2 of Fig.69). Moreover, for the 76:24 mixture, which has a value of α sufficiently close to that of powder with sulphur for these two mixtures to be compared, the value of $\nu \approx 0.28$ lies quite close to the value of ν for black powder, which is $\nu \approx 0.23$ over the range 1 to 1000 atm. Thus it may be expected that the difference in the burning rates of ordinary black powder (with sulphur) and 'sulphurless' powder will be retained even at very high pressures*.

*On the other hand, for 'sulphurless' powder with the proportions 85:15 the value of ν is markedly higher ($\nu \approx 0.50$) than for ordinary powder ($\nu \approx 0.23$). Consequently the difference in the burning rates of these two compositions, which is pronounced at 1 atm ($\approx 2 \text{ mm/sec}$ for 'sulphurless' 85:15 powder, and $\approx 10 \text{ mm/sec}$ for ordinary powder) decreases rapidly with increase of pressure. It is possible that at a pressure of several hundred atmospheres the straight line 3 on Fig.69 ('sulphurless' powder) will intersect the straight line 1 (ordinary powder) and continue above it - in conformity with the heat of combustion. However, the value of α for the 85:15 composition is much closer to the stoichiometric than for the ordinary powder, so that comparison between them is invalid.

The marked acceleration of the combustion of KNO_3 -wood charcoal mixtures by sulphur has not yet been satisfactorily explained, despite the fact that the use of black powder goes back many centuries. Further, it must be emphasized that finely divided wood charcoal is in itself a very reactive fuel:

(1) A stoichiometric KNO_3 -wood charcoal mixture burns very rapidly at 1 atm abs. On the other hand, stoichiometric mixtures of KNO_3 and bitumen, paraffin or graphite will not burn stably at $p \leq 100$ atm (at room temperature) or at $T_0 \leq 200^\circ\text{C}$ (at 1 atm abs).

(2) It is known that mixtures of ammonium nitrate with various organic fuels can burn stably only in the presence of a catalyst (e.g. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$) and at not too low a pressure. However a NH_4NO_3 -wood charcoal mixture at $\alpha = 1$ burns stably even at 1 atm abs (according to the data of A.P. Glazkova). However, the burning rate for this composition is much lower than for similar compositions with KNO_3 or KClO_4 (the burning rates of the compositions indicated are approximately 1, 10 and 14 mm/sec at 25 atm).

(3) The stoichiometric KClO_4 -wood charcoal mixture (see curve 1 of Fig.70) burns at a much higher rate over the pressure range 1 to 24 atm than the KClO_4 -bitumen mixture*. The value of ν for the KClO_4 -wood charcoal mixture for the pressure range investigated ($\nu = 0.44$) is significantly less than that for the KClO_4 -bitumen mixture ($\nu = 0.64$). Therefore at higher pressures a KClO_4 -bitumen mixture may burn more rapidly than a KClO_4 -wood charcoal mixture.

(4) Small additions of wood charcoal can significantly increase the burning rates of a number of condensed systems, and especially those which contain a high excess of fuel (for example, NH_4ClO_4 + perspex, $\alpha = 0.6$)¹⁷⁵.

It is possible to construct approximate curves of $u(\alpha)$ for a KNO_3 -wood charcoal mixture (Fig.71). The maximum burning rate lies near to $\alpha = 0.6$, i.e. significantly closer to the stoichiometric ratio than u_{\max} for a KClO_4 -graphite mixture where u_{\max} lies close to $\alpha = 0.4$ ¹⁷⁵.

*The burning rate of a stoichiometric KClO_4 -wood charcoal mixture at 1 to 25 atm is markedly higher than the burning rate of a similar mixture with KNO_3 , but at the same time is markedly lower than the burning rate of ordinary black powder (with sulphur).

D COMPARISON WITH THEORY

A theoretical expression for the burning rate of black powder as a function of pressure and carbon particle size was first obtained by O.I. Leipunskii⁶⁵. The natural assumption was made that vaporization of the oxidizer takes place first and then the particles of carbon burn in the stream of oxidizer vaporization products above the surface of the charge.

Using the basic supposition that the burning rate is proportional to the square root of the rate of heat release in the reaction zone, by analogy with the Zeldovich-Frank-Kamenetsky theory, see section 1,E, an expression was obtained for the burning rate of finely divided* powder. For the diffusion regime of burning of carbon particles the burning rate of the powder is $u \sim \sqrt{p/d}$, and for the kinetic regime, with a first-order reaction, $u \sim p/\sqrt{d}$.

It has been shown that the experimental value of ν is close to unity for pressure below atmospheric and is close to $\nu = 0.5$ for pressures of several atmospheres, and for higher pressures the experimental value of ν decreases. It can be assumed that the value $\nu \approx 1$ in a vacuum corresponds to the kinetic regime, and the value $\nu \approx 0.5$ at 1 to 5 atm to the diffusion regime. The decrease of ν at higher pressures was not explained in Ref.65. However it can be understood if the concept of the zone of influence (see section 10,B) is introduced. With increasing pressure, the size of the zone of influence decreases more and more rapidly and the velocity of the fuel particles, the size remaining constant, falls more and more rapidly below the velocity of the gas. At very high pressures the particles inside the boundary of the zone of influence are practically stationary. In this case, as in section 8,B, the burning rate does not depend on pressure, i.e. $\nu = 0$.

The effect of the particle size of carbon on the burning rate (the dependence $u(d)$) has scarcely been investigated experimentally. However, exploratory experiments¹³⁷ indicate that the experimental dependence $u(d)$ is much less⁶ than $u \approx d^{-1}$.

*The particle size d of the carbon particles is so small that their velocity can be taken as equal to the gas velocity.

⁶Two mixtures of identical composition (85% KNO_3 + 15% wood charcoal) were investigated. In one mixture the size of the particles of fuel and oxidizer was ≈ 10 to 20μ , in the other $\approx 400 \mu$. At 1 to 50 atm the burning rate of the finely divided mixture was only approximately twice that of the coarse mixture (at 50 atm, $u_{fi} \approx 16$ mm/sec, $u_{co} \approx 8$ mm/sec), although the particle sizes differed by a factor of ten.

B.V. Novozhilov²²⁵, who continued the work of Ref.65, attempted to obtain a solution without making the assumption that the particles of carbon move with the velocity of the gas. For the kinetic regime $u \approx p/d^{1/3}$ was obtained, and for the diffusion regime $u \approx p^{1/3}/d$.

However in later work, B.V. Novozhilov²²⁶ acknowledged that the above results were incorrect in that the calculation of the entrainment of the particles by the gas stream was made inaccurately and for the diffusion regime he returned to the expression $u \approx \sqrt{p/d}$ obtained in Ref.65.

An attempt was also made²²⁶ to calculate the absolute burning rate of black powder, using the assumption that the ignition temperature of the particles of carbon could be calculated by means of the Frank-Kamenetsky criterion. The calculated value of the burning rate proved to be considerably lower than the experimental value. Hence the conclusion was drawn that the particles of carbon ignite earlier than follows from this criterion.

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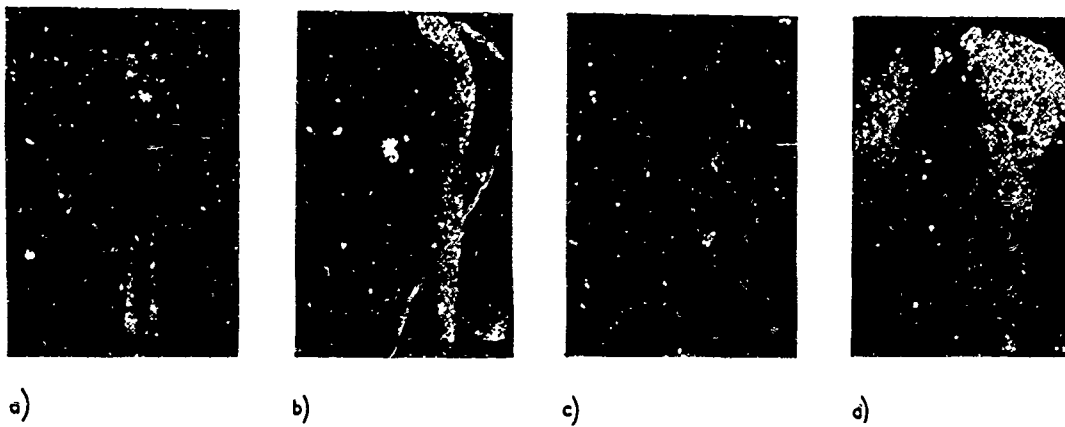


Fig. 1 Laminar (a, b) and turbulent (c, d) flames of a stoichiometric mixture of natural gas and air⁵⁰

a, c - ordinary photograph with long exposure

b, d - schlieren photograph with very short exposure

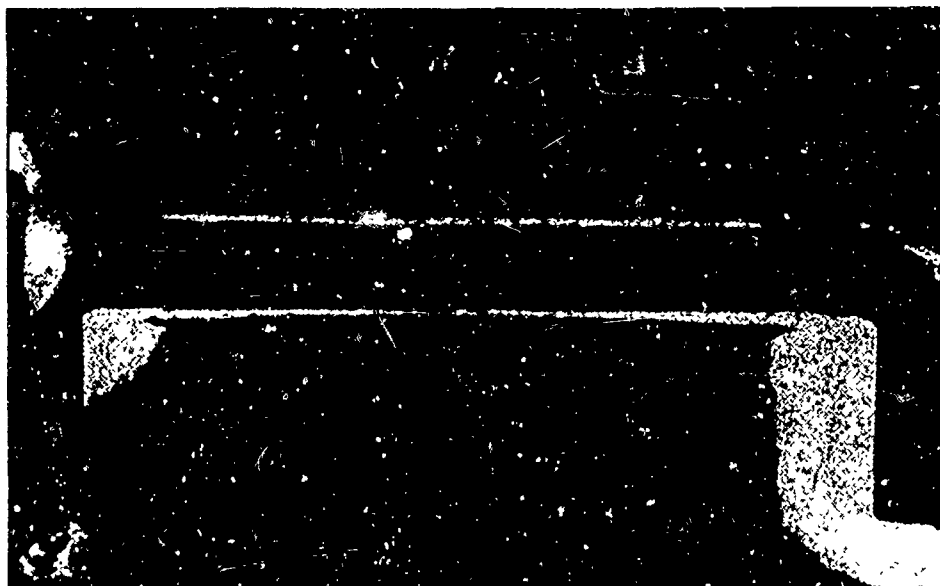


Fig. 2 Ethylene-air flame on a flat-flame burner²⁰

The gas velocity is traced by means of fine particles
(~ 4 micron)

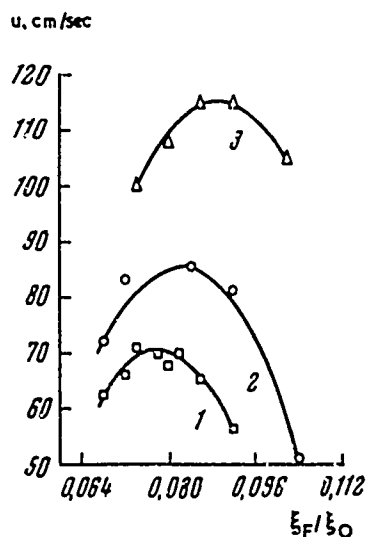


Fig. 3 Dependence of burning rate on oxidizer/fuel ratio for mixtures of (1) propane (2) propylene (3) propyne with air at $p = 1$ atm abs.¹⁵

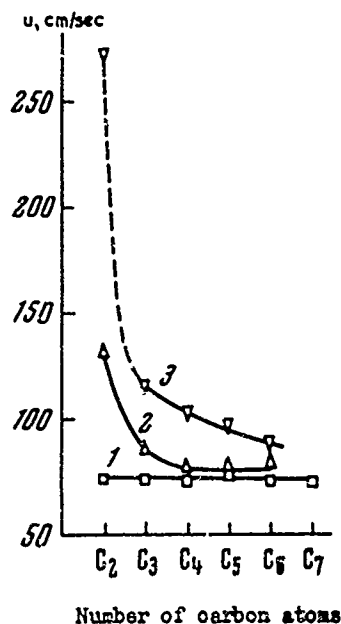


Fig. 4 Maximum burning rate in air mixtures of (1) n-alkanes (2) n-alkenes (3) n-alkynes in dependence on length of chain.¹³

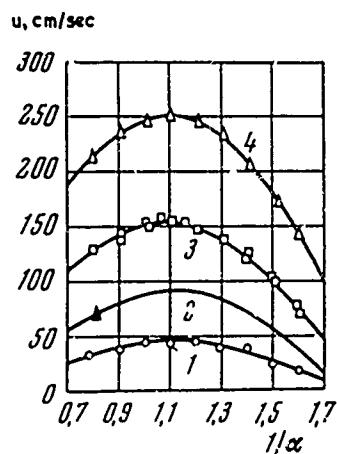


Fig. 5 Dependence of linear burning rate of C_2H_2 -air mixture on ratio of components ($1/\alpha$) at various initial temperatures ($p = 1$ atm abs.)²¹
1 - 311.0°K
2 - 477.5°K
3 - 644.3°K
4 - 811.0°K

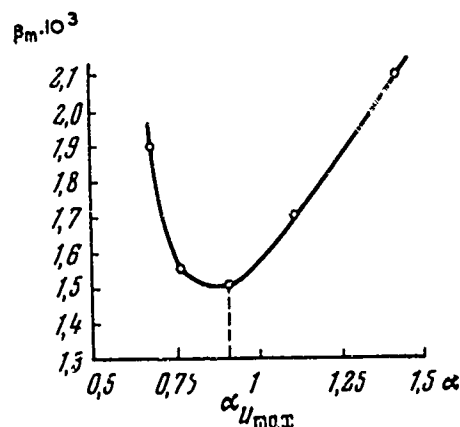


Fig. 6 Dependence of temperature coefficient $\beta_m = d \ln m / d T_0 \text{ deg}^{-1}$ on ratio of components α for C_2H_2 -air mixtures.²¹ Position of maximum burning rate shown by dotted vertical line

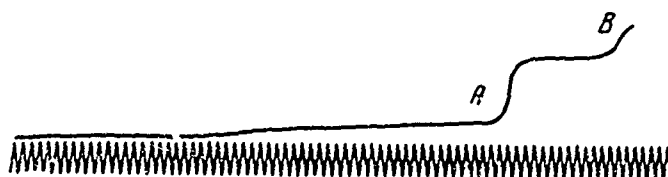


Fig. 7 Temperature profile in combustion zone at $p = 5.7$ atm abs
(thermocouple W + 5% Re, W + 20% Re; $\phi = 30\mu$)⁴⁷
Portion A = first flame; Portion B = second flame

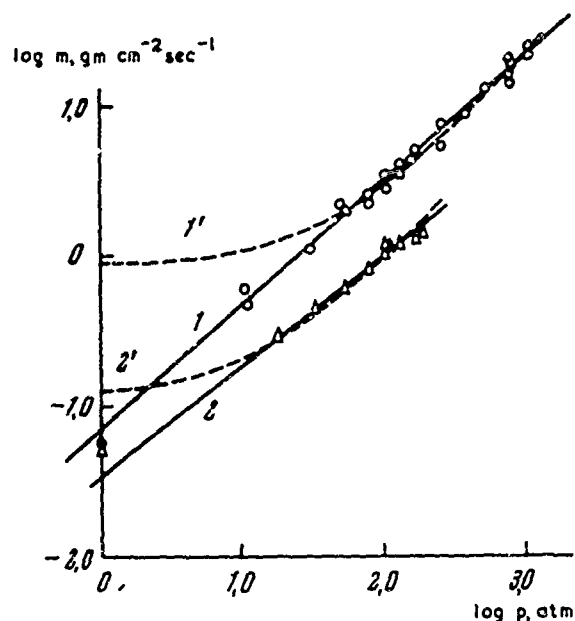
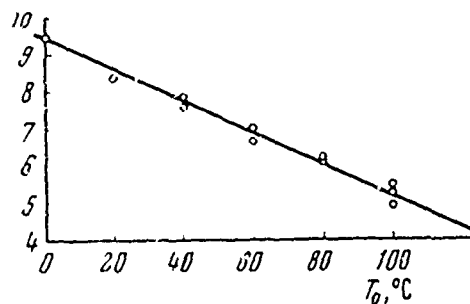
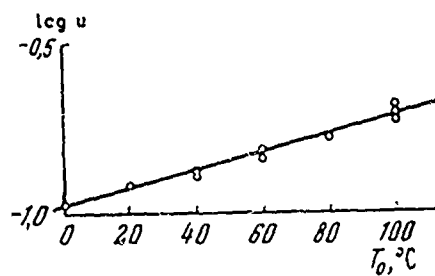


Fig. 8 Dependence $m = f(p)$ (m , $\text{gm cm}^{-2}\text{sec}^{-1}$; p , atm) for cyclonite (RDX) Δ and dynamite Δ ⁴²
1 - straight line $m = 0.072 p^{0.82}$ 2 - straight line $m = 0.034 p^{0.74}$
1' - curve $m = 0.9 + 0.0216 p$ 2' - curve $m = 0.118 + 0.009 p$
• - our data for $p = 1$ atm abs

$1/u$, sec/cm



(a) $1/u \sim T_0$



(b) $\log u \sim T_0$

Fig. 9 Dependence of burning rate of gelatinized nitroglycerine (with 3% addition of collodion) on initial temperature at atmospheric pressure³⁵

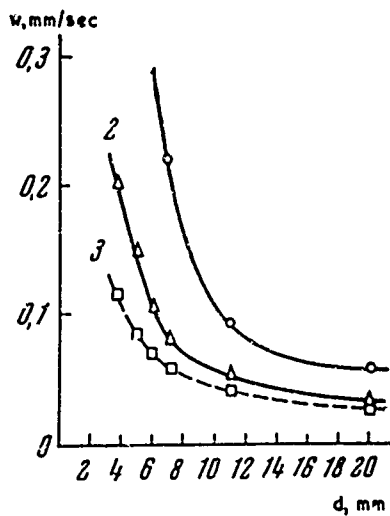
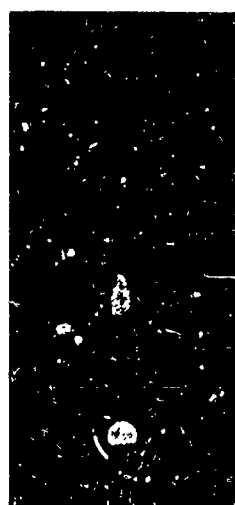
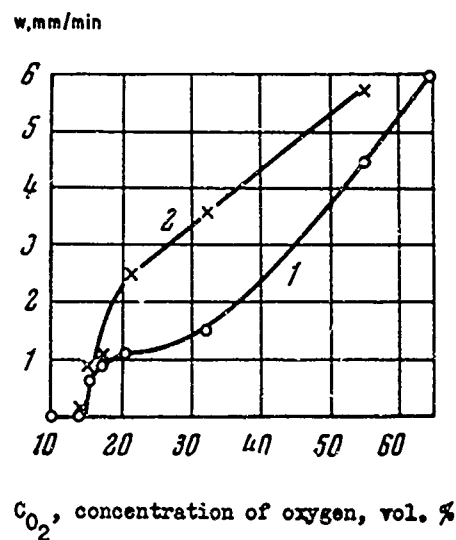


Fig. 10 Dependence of burning velocity of liquids w on diameter of test tube d ⁵¹

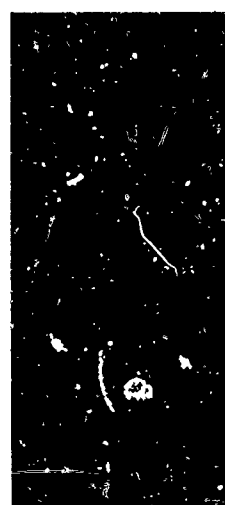
1 - car petrol
2 - tractor kerosene
3 - diesel fuel

Fig. 11 Dependence of burning rate of liquids w on concentration of oxygen at $p = 1 \text{ atm abs}$ ⁴⁹

1 - diesel fuel
2 - petrol



(a) $p = 650 \text{ mm Hg}$



(b) $p = 240 \text{ mm Hg}$

Fig. 12 Burning of ethyl alcohol in air on a porous sphere at pressures of 650 and 240 mm Hg⁵⁴



Fig. 13 Tracks of aluminium particles ($30-35\mu$) burning at $p = 1 \text{ atm abs}$ in a stream of gas ²²⁸
Temperature and composition of gas
a) $T = 2390^\circ\text{K}$, 34% O_2 , 0.6% H_2O
b) $T = 2410^\circ\text{K}$, 32% O_2 , 17% H_2O
The fragmentation of particles can be seen at the end of the tracks

a)

b)

Fig. 14 Ciné frames (3800 frame/sec) of burning of aluminium particles above surface of powder ($p = 14 \text{ atm}$)⁶

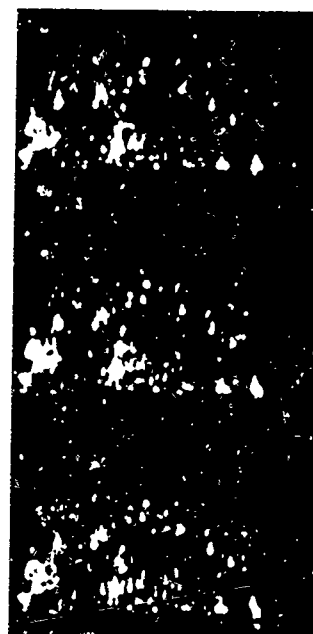


Fig. 15 'Disruption' of burning particles of titanium⁶¹
particle size $150-420\mu$; burning in oxygen; ignition by gas flame

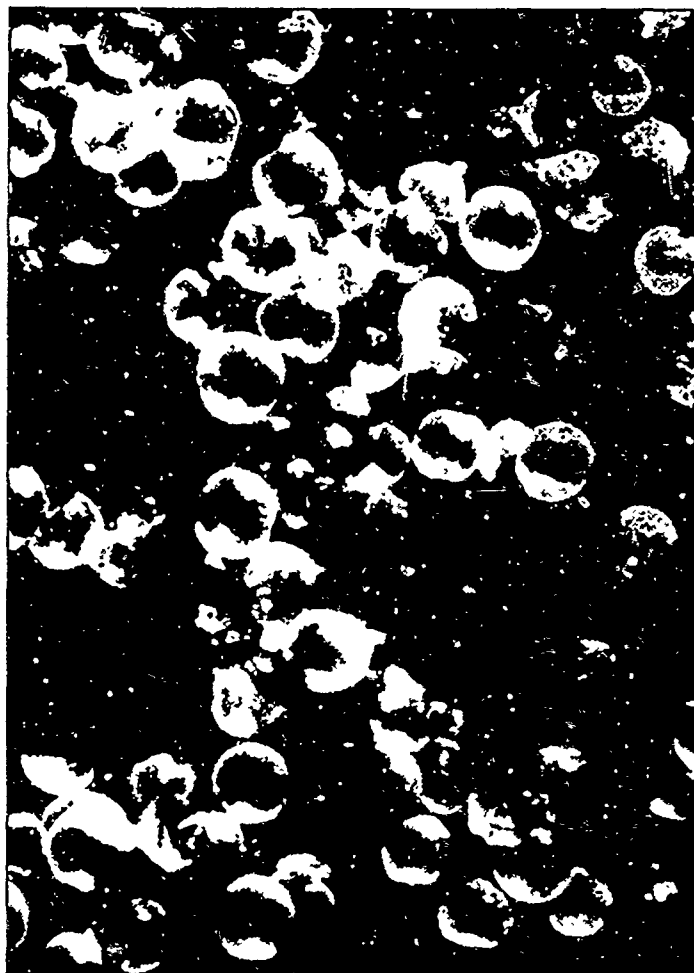


Fig. 16 Spheres of Al_2O_3 ($d \approx 150\mu$) formed during the burning of aluminium particles ($d = 70\mu$)²²⁹
Some of the spheres have disintegrated showing that they are hollow

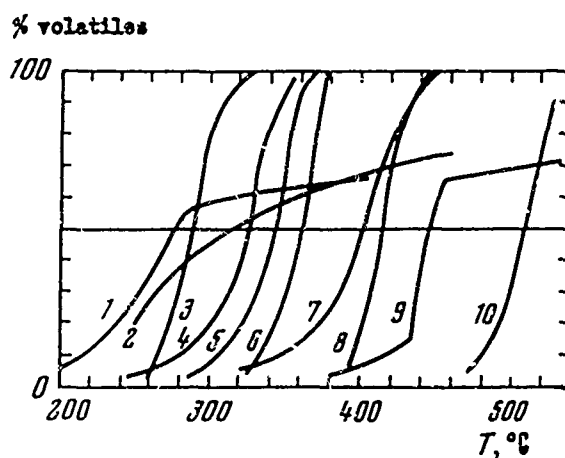


Fig. 17 Degree of vaporization of polymers (% volatiles in relation to initial polymer) on heating for 30 minutes in vacuo at the temperature indicated¹²⁸

- | | |
|--------------------------|----------------------------|
| 1 polyvinyl chloride | 6 polystyrene |
| 2 polyacrylonitrile | 7 polybutadiene |
| 3 polymethylstyrene | 8 polymethylene |
| 4 polymethylmethacrylate | 9 polyvinylidene fluoride |
| 5 polymethylisobutylene | 10 polytetrafluoroethylene |

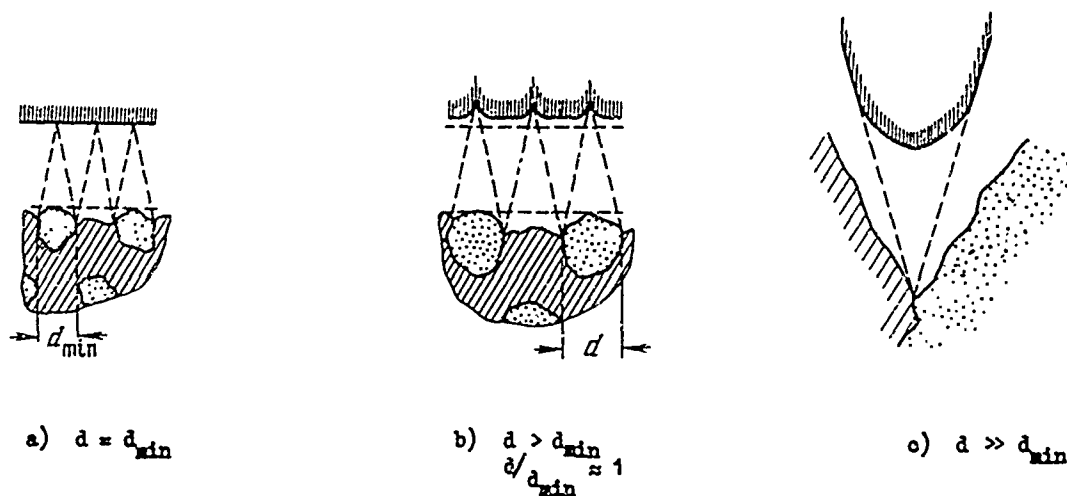


Fig. 18 Schematic view of combustion front and surface of charge for condensed mixtures

Fig. 19 Burning of spherical particles of NH_4ClO_4 in a block of poly-methylmethacrylate²³²

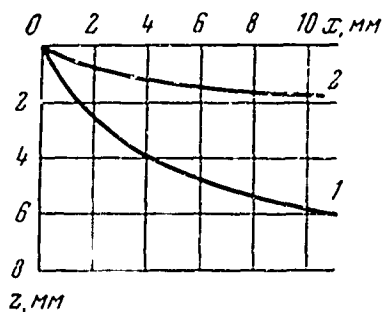


Fig. 20 Mean profile of indentation formed in a plate of perspex burning in contact with KClO_4 ($\delta = 0.68$) at 1 atm abs¹²⁴

x = distance along length of plate
 z = depth of burning, origin of coordinates at 'tip' of flame

1 - $d_{\text{KClO}_4} = 25 \text{ mm}$; $u = 0.50 \text{ mm/sec}$

2 - $d_{\text{KClO}_4} = 3.8 \text{ mm}$; $u = 0.98 \text{ mm/sec}$

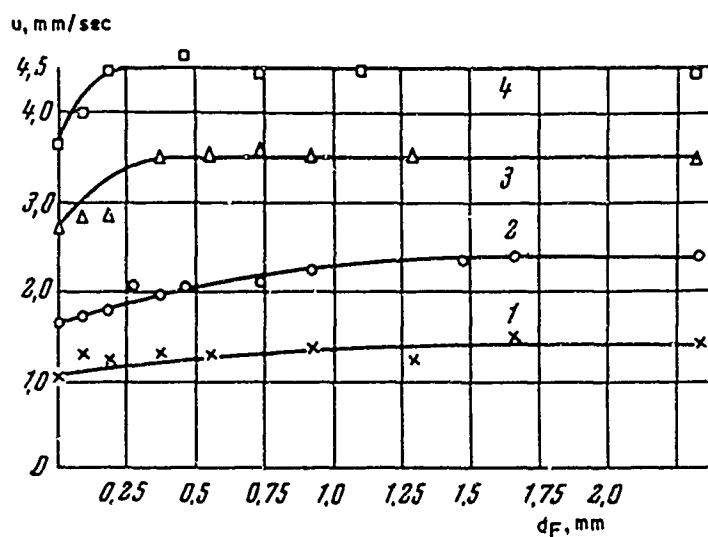
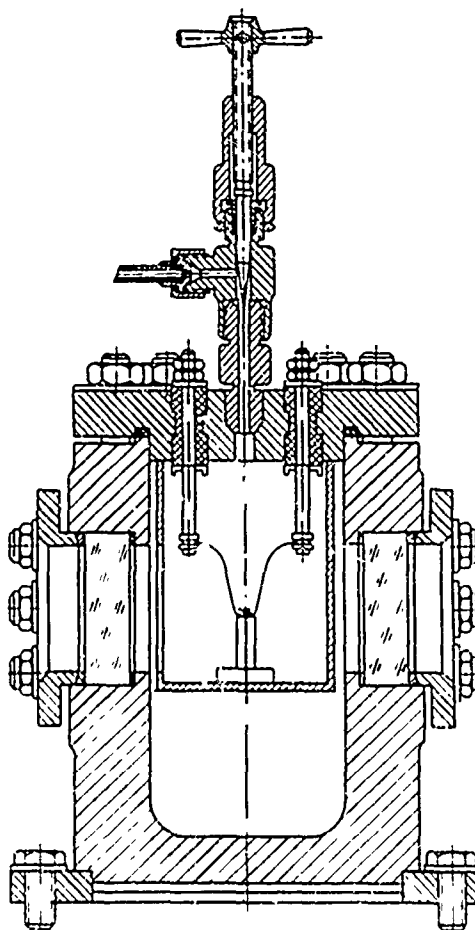


Fig. 21 Velocity of flame, u , in system: layer $KClO_4$ ($\delta = 0.68$) + film of polyethylene of various thicknesses, d_F , + thick substratum of perspex at various pressures¹²⁴
 1 - 5 atm (gauge); 2 - 10 atm (gauge); 3 - 20 atm (gauge);
 4 - 30 atm (gauge)

Fig. 22 Schematic diagram of constant pressure bomb B-150



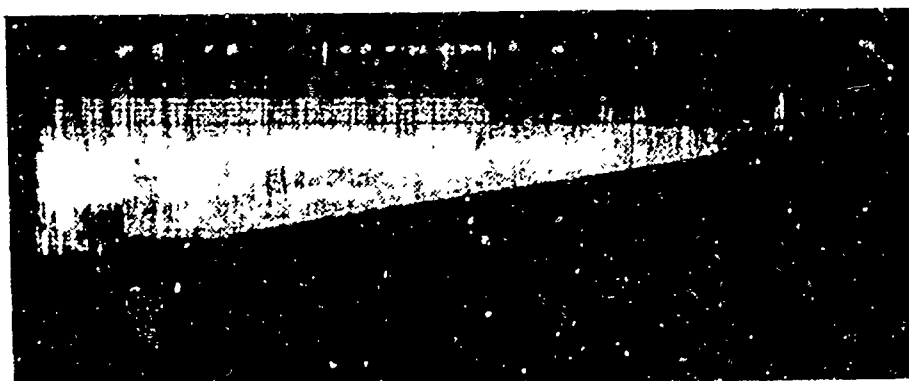


Fig. 23 Sample of drum camera record

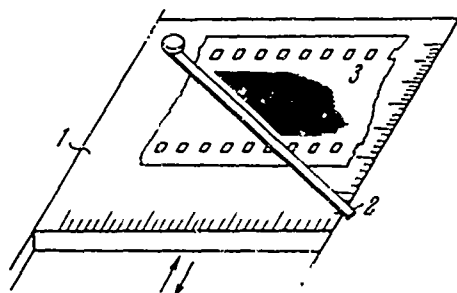


Fig. 24 Appliance for evaluating
film records made by
photorecorder
1 - sliding plate
2 - ruler pivoting around
pin
3 - film record

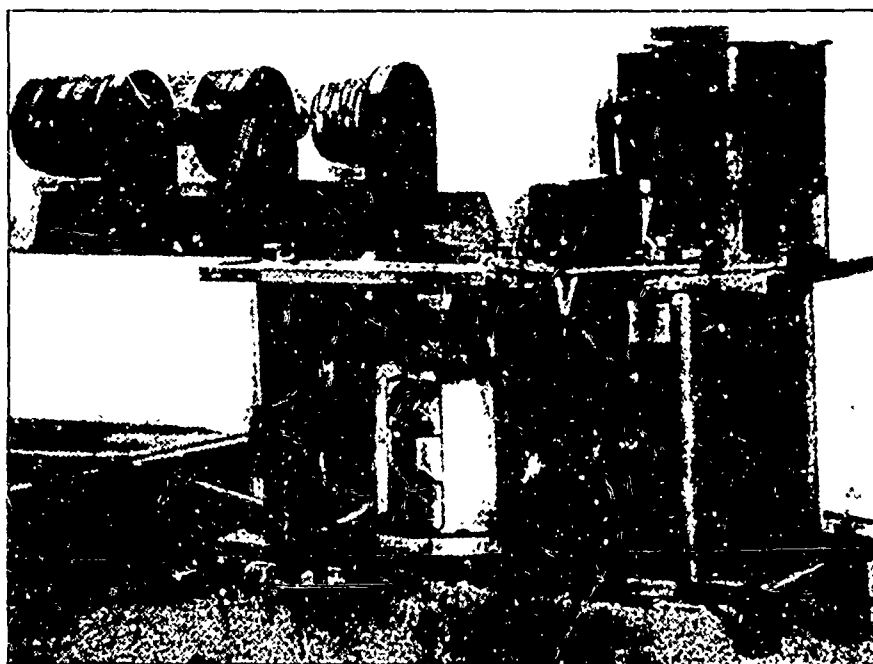


Fig. 25 Drum camera with double-objective optical system
for measuring burning rate

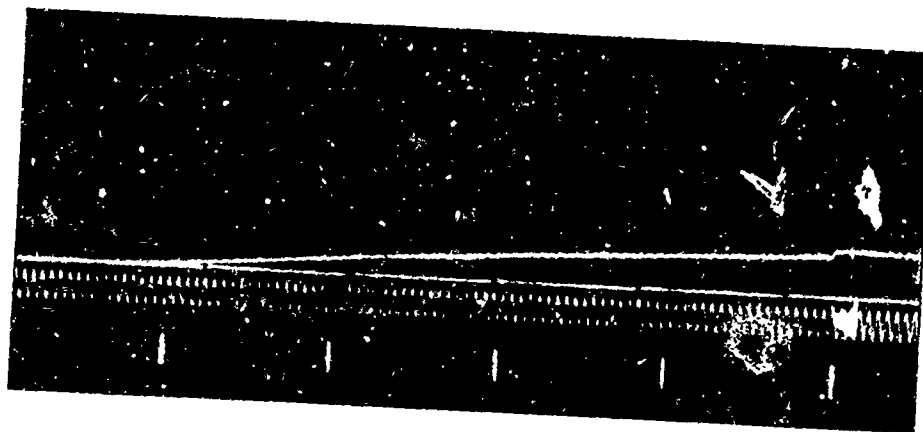


Fig. 26 Oscillogram with record of $p(t)$ curve
lower trace - time marker (~ 50 c/s from mains supply)
middle trace - zero line, which also shows time marks of multiple frequency (X8 or X16 or X32 etc) to facilitate evaluation of record
upper trace - record of increase of pressure in bomb during burning

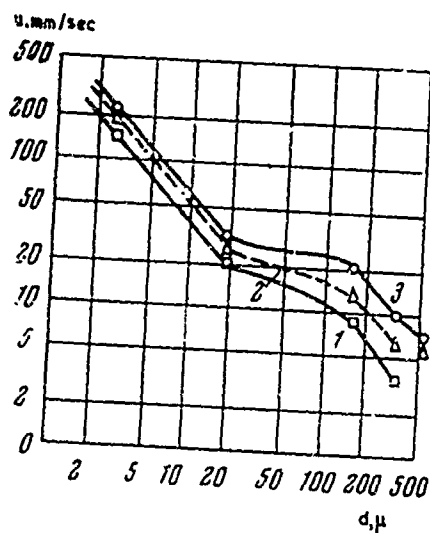
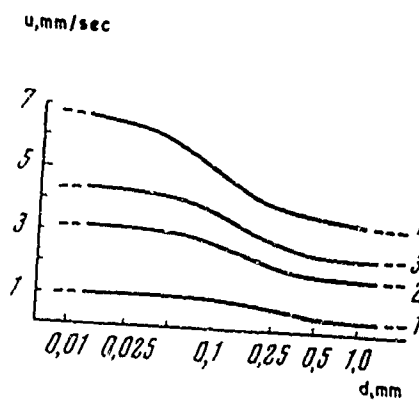


Fig. 27 Dependence of burning rate of mixture 90% W + 10% KClO_4 on tungsten particle size (d) at different pressures¹³⁹

1 - 10 atm
2 - 2-50 atm
3 - 100 atm

Fig. 28 Dependence of burning rate of stoichiometric mixture KClO_4 + bitumen on oxidizer particle size (d) at different pressures¹³⁷

1 - 1 atm abs 3 - 5 atm abs
2 - 3 atm abs 4 - 10 atm abs



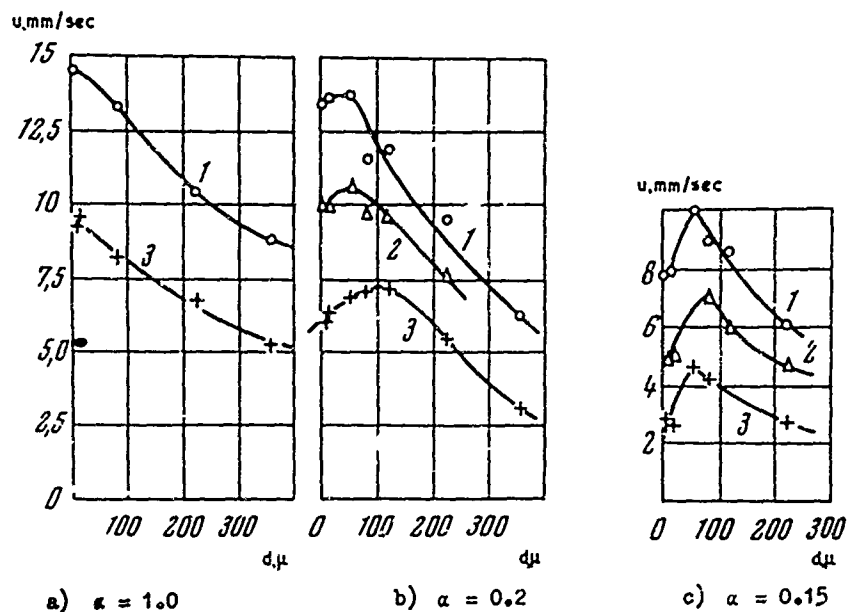


Fig. 29 Dependence of burning rate on NH_4ClO_4 particle size (d) for ungelatinized mixtures NH_4ClO_4 + polystyrene ($< 100\mu$) at various pressures¹⁷⁰

1 - 100 atm 2 - 70 atm 3 - 40 atm

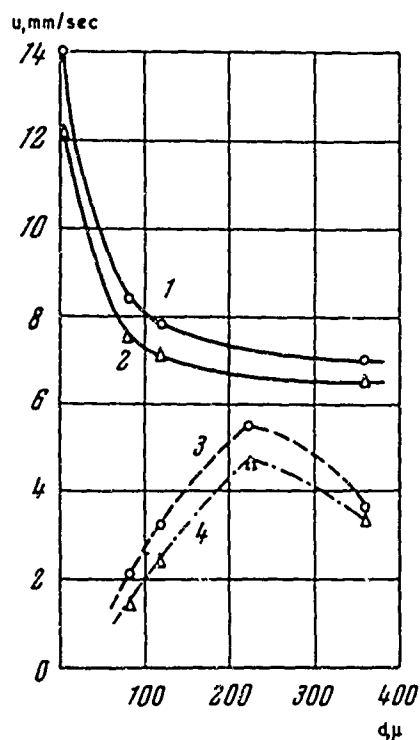


Fig. 30 Dependence of burning rate on NH_4ClO_4 particle size (d) for ungelatinized mixtures NH_4ClO_4 + perspex ($\sim 3\mu$) at various pressures¹⁷⁰

1, 2 - $\alpha = 1$
3, 4 - $\alpha = 0.2$
o 100 atm
 Δ 70 atm

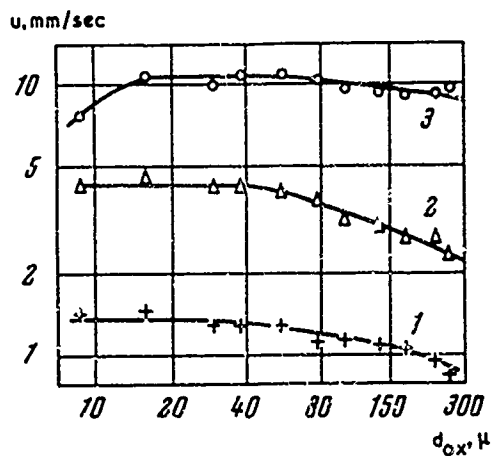


Fig. 31 Dependence of burning rate on oxidizer particle size (d_{ox}) for Thiokol composition at different pressures¹⁷⁸

1 - 1.2 atm
2 - 7 atm
3 - 112 atm

Fig. 32 General form of dependence $u(\alpha)$ for finely divided (u_{f1}) and coarse (u_{co}) mixtures

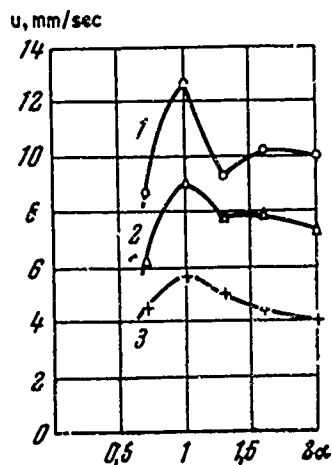
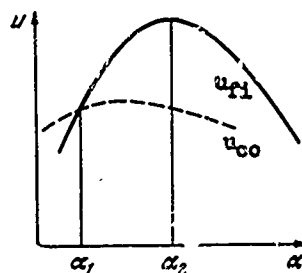
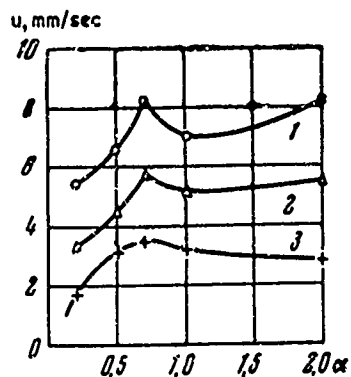


Fig. 33 Dependence $u(\alpha)$ for ungelatinized mixture NH_4ClO_4 ($\sim 5 \mu$) + perspex ($\sim 3 \mu$) at different pressures¹⁷⁵

1 - 100 atm
2 - 40 atm
3 - 10 atm

Fig. 34 Dependence $u(\alpha)$ for ungelatinized mixture NH_4ClO_4 (140-320 μ) + perspex ($\sim 3 \mu$) at different pressures¹⁷⁵

1 - 100 atm
2 - 40 atm
3 - 10 atm



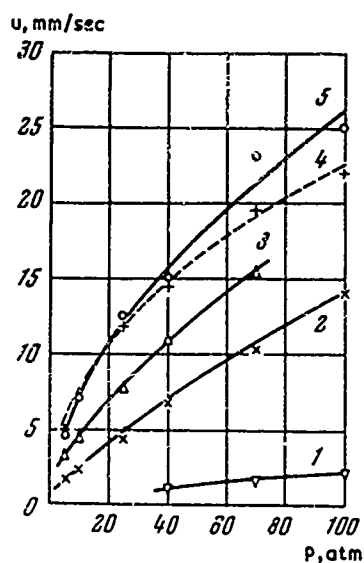


Fig. 35 Dependence $u(p)$ for gelatinized mixture NH_4ClO_4 ($\sim 40\mu$) + polystyrene for various values of α ¹⁷⁵

- 1 - $\alpha = 0.1$
- 2 - $\alpha = 0.2$
- 3 - $\alpha = 0.3$
- 4 - $\alpha = 0.5$
- 5 - $\alpha = 1$

Fig. 36 Dependence $u(p)$ for mixture 10% KClO_4 + 90% W ($\alpha \approx 0.2$) for various tungsten particle sizes¹³⁹

- 1 - 2.7μ
- 2 - 19μ
- 3 - 160μ
- 4 - 340μ
- 5 - 550μ

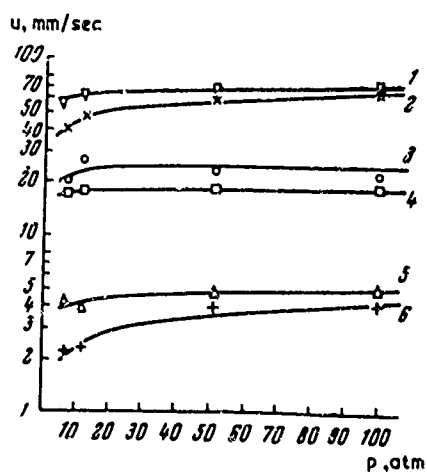
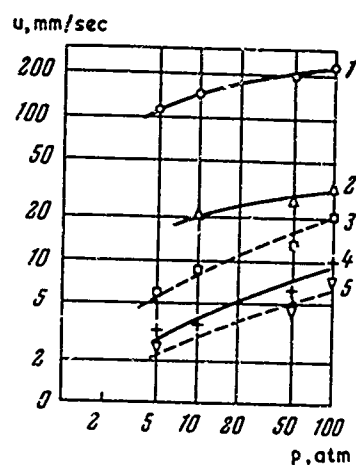
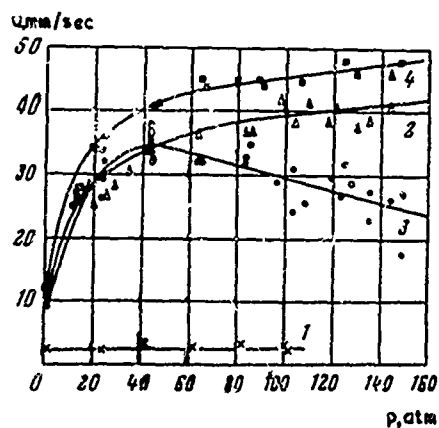


Fig. 37 Dependence $u(p)$ for mixture $\text{Al} + \text{Fe}_2\text{O}_3$ ($\alpha \approx 1$) for various aluminium particle sizes (d_{Al}) and various charge diameters (ϕ)¹³⁹

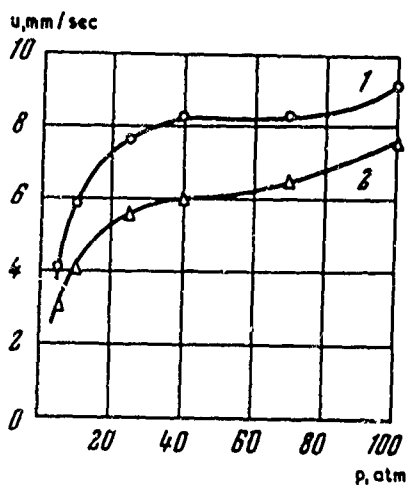
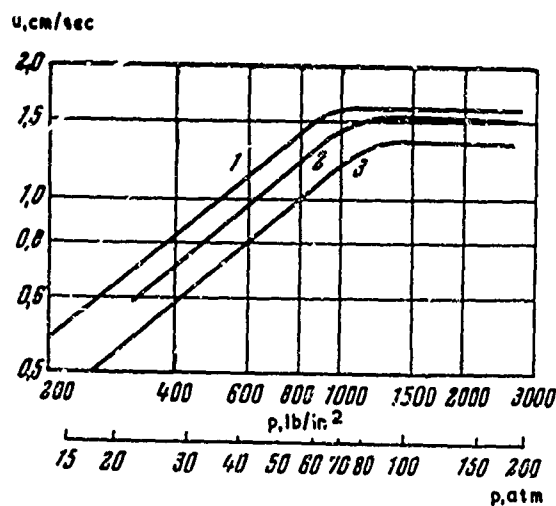
- 1 - $d_{\text{Al}} = \sim 0.1\mu$, $\phi = 6.0\text{ mm}$
- 2 - $d_{\text{Al}} = \sim 3\mu$, $\phi = 6.0\text{ mm}$
- 3 - $d_{\text{Al}} = \sim 12\mu$, $\phi = 10.0\text{ mm}$
- 4 - $d_{\text{Al}} = \sim 12\mu$, $\phi = 6.0\text{ mm}$
- 5 - $d_{\text{Al}} = \sim 170\mu$, $\phi = 10.0\text{ mm}$
- 6 - $d_{\text{Al}} = \sim 540\mu$, $\phi = 10.0\text{ mm}$

Fig. 38 Dependence $u(p)$ for a number of thermite mixtures¹⁵⁷

- 1 - x, $\text{Cr}_2\text{O}_3 + 2 \text{Al}$
 2 - Δ , Δ , $\text{Fe}_2\text{O}_3 + 2 \text{Al}$
 3 - o, o, $\text{Cr}_2\text{O}_3 + 3 \text{Mg}$
 4 - ■, $3 \text{MnO}_2 + 4 \text{Al}$
 x, o, Δ , ■ - experiments in nitrogen
 o, Δ - experiments in argon

Fig. 39 Dependence $u(p)$ for mixtures NH_4ClO_4 (76-104 μ) + paraformaldehyde (<76 μ) for various values of α ¹⁴¹

- 1 - $\alpha = 2.23$
 2 - $\alpha = 1.0$
 3 - $\alpha = 0.64$

Fig. 40 Dependence $u(p)$ for gelatinized mixture NH_4ClO_4 + perspex ($\alpha = 0.7$)¹⁶⁸

- NH_4ClO_4 particle size
 1 - 80% (~5 μ) + 20% (140-320 μ)
 2 - 50% (~5 μ) + 50% (140-320 μ)

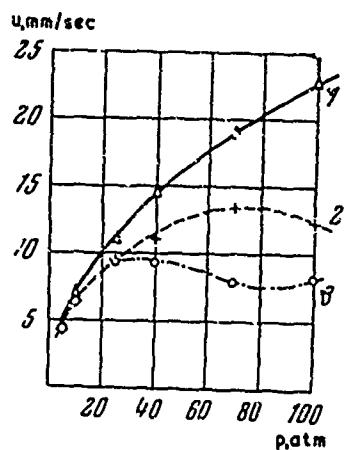


Fig. 41 Dependence $u(p)$ for gelatinized mixture NH_4ClO_4 ($\sim 5\mu$) + perreper¹⁷⁵
 1 - $\alpha = 1$
 2 - $\alpha = 0.7$
 3 - $\alpha = 0.6$

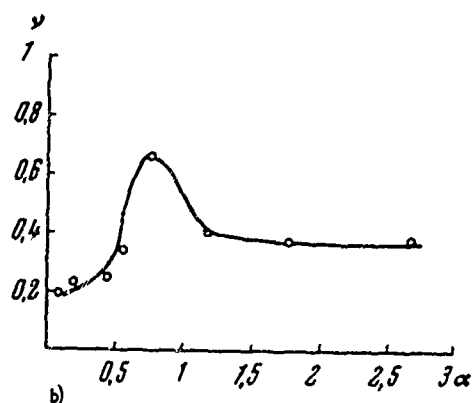
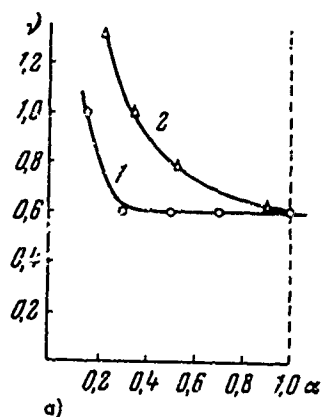


Fig. 42 Dependence $v(\alpha)$ (at $p = 5$ to 100 atm)

a) Type I curve (ref. 175)

1 - NH_4ClO_4 ($\sim 40\mu$) + polypropylene ($< 100\mu$)
 2 - KClO_4 ($\sim 10\mu$) + urotropine (finely divided)

b) Type II curve (ref. 164)

KClO_4 ($\sim 10\mu$) + tungsten ($\sim 3\mu$)

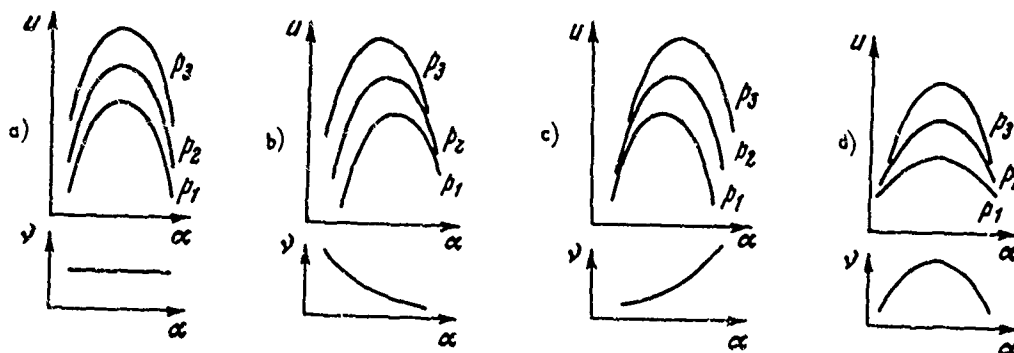


Fig. 43 Effect of position of maximum and shape of curve $u(\alpha)$ at different pressures on nature of dependence $v(\alpha)$

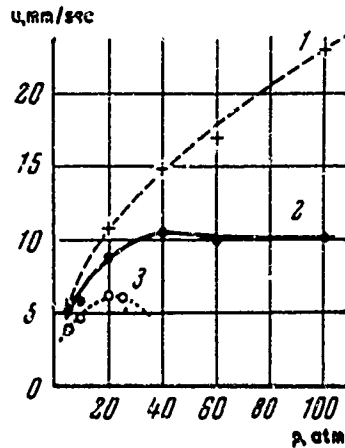


Fig. 44 Dependence $u(p)$ for gelatinized mixture NH_4ClO_4 ($\sim 5\%$) + perspex ($\alpha = 0.5$) for various initial temperatures:

- 1 - 150°C
- 2 - 75°C
- 3 - 20°C

Fig. 45 Effect of additives on dependence $u(p)$ for gelatinized mixture NH_4ClO_4 ($\sim 5\%$) + perspex ($\alpha = 0.6$) (ref. 175)

- 1 - 0, without additive
- 2 - ∇ , 2% polystyrene, gelatinized with mixture; a mixture with 2% wood charcoal gives practically the same burning rate, +
- 3 - \times , 2% Cu_2O

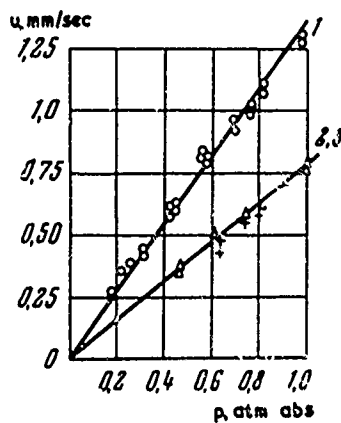
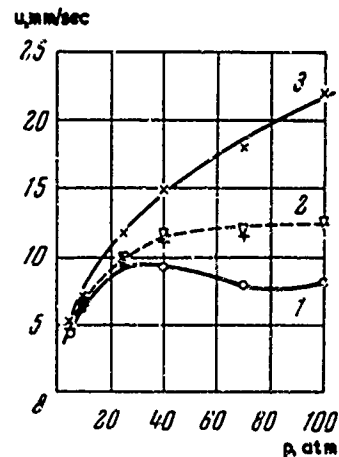


Fig. 46 Dependence of burning rate of finely divided mixtures on pressure at $p < 1 \text{ atm abs}$:

- 1 - 0, NH_4ClO_4 + bitumen ($\alpha = 1$)
- 2 - Δ , NH_4ClO_4 + trotyl (TNT) ($\alpha = 1$)
- 3 - $+$, KClO_4 + trotyl (TNT) ($\alpha = 1$)

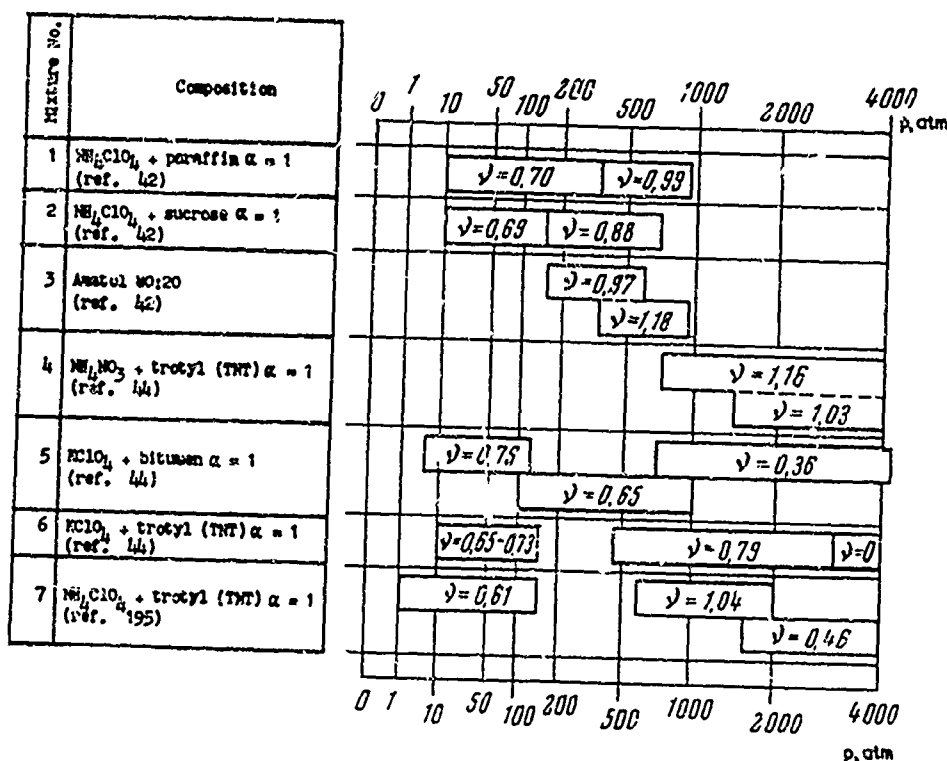


Fig. 47 Value of exponent ν in equation $u = bp^\nu$ for some condensed mixtures over various pressure ranges

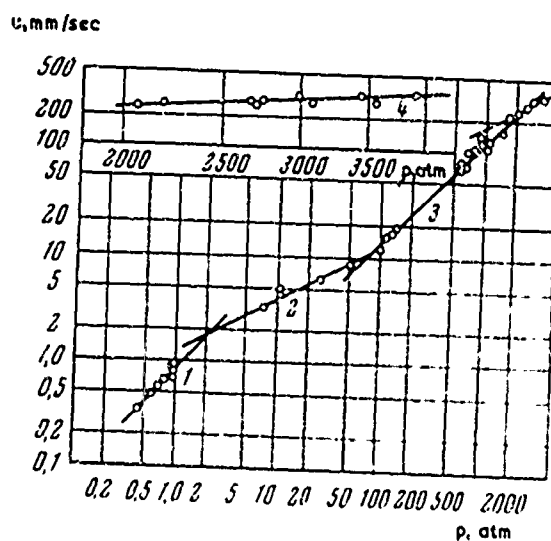


Fig. 48 Dependence $u(p)$ for mixtures of finely divided NH_4ClO_4 and trotyl (TNT) ($\alpha = 1$) (ref. 195)
Data in the range 2000-4000 atm (straight line 4) are given in inset on a much larger scale for p axis

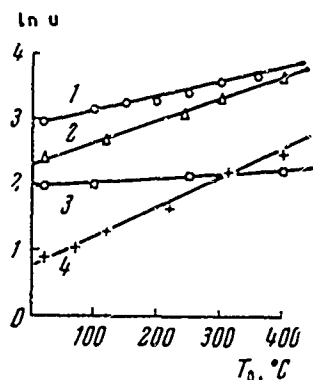


Fig. 49 Dependence of burning rate on initial temperature T_0 for some thermitic mixtures¹⁶⁵

- 1 - Al-Fe₂O₃ ($\alpha = 1$)
- 2 - B-Fe₂O₃ ($\alpha = 1$)
- 3 - Mg-Fe₂O₃ ($\alpha = 1$)
- 4 - W-KClO₄ ($\alpha = 1.78$)

Fig. 50 Dependence of burning rate on initial temperature T_0 for ungelatinized NH₄ClO₄ + polystyrene mixture ($\alpha = 1.5$) (ref. 216)

- 1 - $d_{ox} \approx 10 \mu$
- 2 - $d_{ox} = 140-320 \mu$

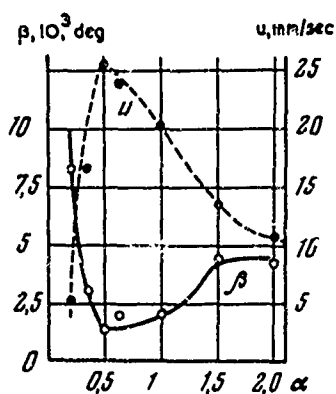
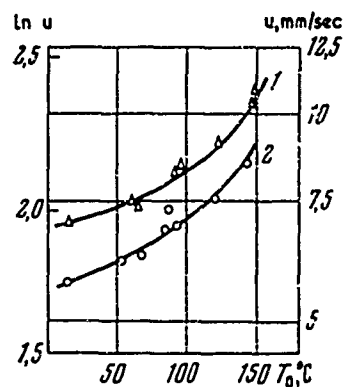
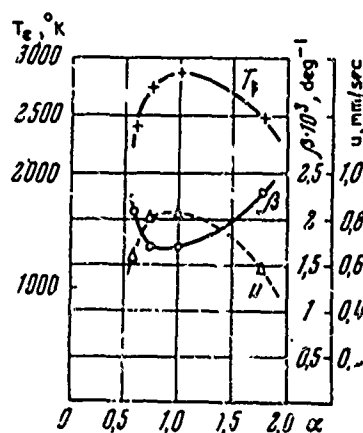
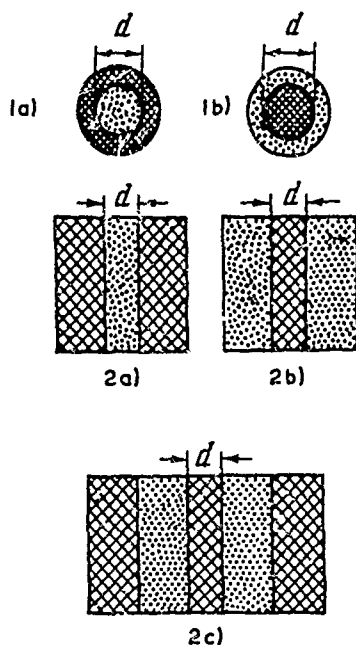


Fig. 51 Dependence of temperature coefficient p and burning rate u on α for gelatinized NH₄ClO₄ ($\sim 10 \mu$) + polystyrene mixture; $p = 40$ atm (ref. 216)

Fig. 52 Dependence of temperature coefficient p , burning rate u , and equilibrium combustion temperature T_e (calculated) on α for finely divided NH₄ClO₄ + polyformaldehyde mixture at atmospheric pressure



Fig. 53 Configurations of layer systems^{124,127,166}

- 1a) Cylindrical core of oxidizer in co-axial tube of fuel
 1b) Cylindrical core of fuel in coaxial tube of oxidizer
 2a) Oxidizer layer between two fuel layers
 2b) Fuel layer between two oxidizer layers
 2c) As 2b, but with additional fuel layer on each external face

Fig. 54 Dependence of burning rate u on thickness d of oxidizer¹²⁴
 1 - $KClO_4$ layer ($\delta \sim 0.92$) between two perspex layers ($p = 20$ atm), Δ
 2 - $KClO_4$ ($\delta = 0.62-0.67$) between two layers, 0; in cylindrical perspex tube, \circ , ($p = 10$ atm)
 3 - BaO_2 ($\delta = 0.35$) in plane channel in perspex ($p = 20$ atm), +

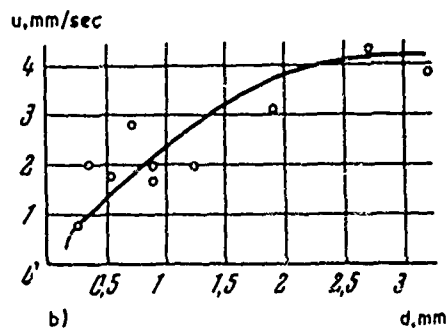
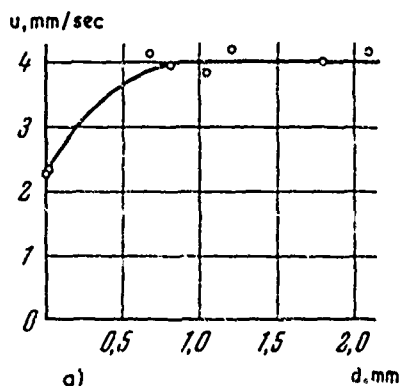
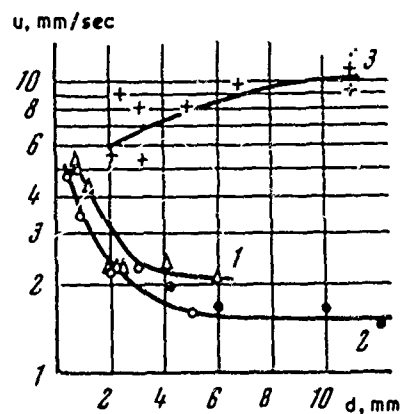


Fig. 55 Dependence of burning rate u on thickness d of fuel layer between two $KClO_4$ layers ($p = 20$ atm) (ref. 124)
 a) - Perspex; configuration 2c of Fig. 53, $\delta_{KClO_4} = 0.92$
 b) - Polyethylene; configuration 2b of Fig. 53, $\delta_{KClO_4} = 0.84$

Fig. 56 Dependence $u(p)$ for various oxidizers in coaxial tube (dia. 6 mm) of perspex¹²⁷

- 1 - $KClO_4$ ($\delta = 0.84-0.88$)
- 2 - $KClO_3$ ($\delta = 0.85-0.89$)
- 3 - BaO_2 ($\delta = 0.33-0.34$)
- 4 - $KMnO_4$ ($\delta = 0.53-0.56$)
- 5 - Stoichiometric ungelatinized $KClO_4$ + perspex mixture; predominating particle size $< 10\mu$

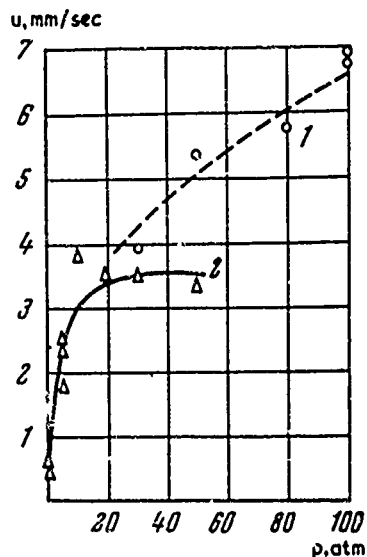
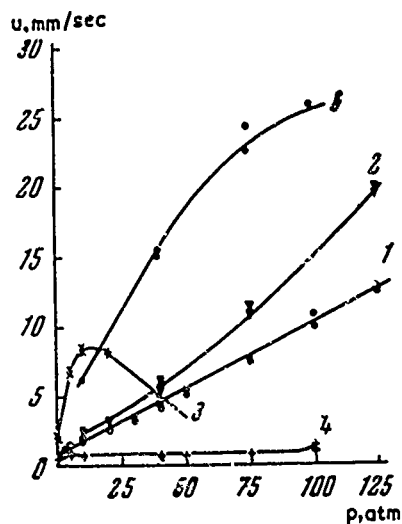


Fig. 57 Dependence $u(p)$ for cylindrical core (dia. 6 mm) of fuel in coaxial tube of oxidizer¹⁶⁶

- 1 - Al (powder, $\delta \approx 0.94$) - $Ba(NO_3)_2$
- 2 - W (particle size 140-400 μ ; $\delta \approx 0.40-0.45$) - $KMnO_4$ ($\delta \approx 0.94$)

Fig. 58 Dependence $u\delta = f(\delta)$ for $KClO_4$ in cylindrical tube (dia. 6 mm) of perspex at various pressures¹²⁴

- 1 - 40 atm
- 2 - 5 atm

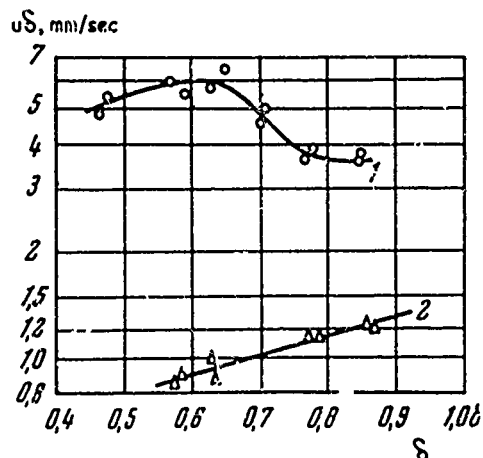


Fig. 59 Dependence $u\delta = f(\delta)$ for a cylindrical core (dia. 6 mm) of aluminium powder in a coaxial tube of KNO_3 ($\delta = 0.94$) at 20 atm (ref. 166)

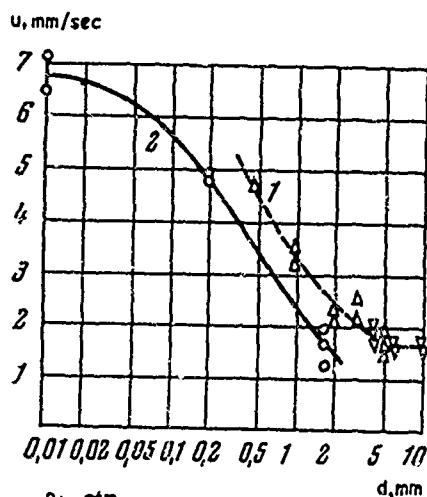
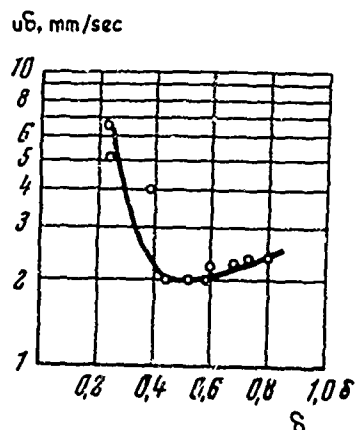


Fig. 60 Comparison of dependence $u(d)$ for layer system and ordinary disordered mixture^{124, 127}

1 - $KClO_4$ layer ($\delta = 0.62-0.67$) of thickness d in perspex ($p = 10$ atm) Δ plane layer ∇ cylindrical core
2 - gelatinized $KClO_4$ + perspex mixture ($\alpha = 1$; $p = 10$ atm; $\delta \approx 0.9$)

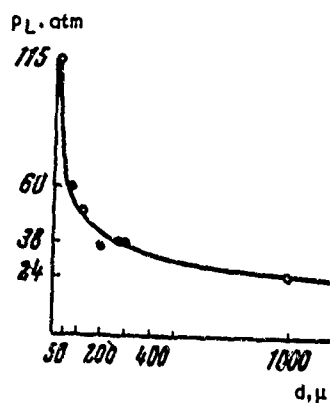


Fig. 61 Dependence of p_L (pressure at lower limit) on approximate mean particle size d of NH_4ClO_4 (ref. 189)

Experiments in constant pressure bomb; uncoated charges 8 mm dia; $\delta \approx 0.98$

Fig. 62 Dependence $u(p)$ for NH_4ClO_4 (not fractionated) in perspex tubes (internal dia. ϕ ; wall thickness 1 mm; $\delta_{NH_4ClO_4} > 0.91$) (ref. 121)

$\Delta - \phi = 5$ mm
 $0 - \phi = 7$ mm
 $+ - \phi = 10$ mm

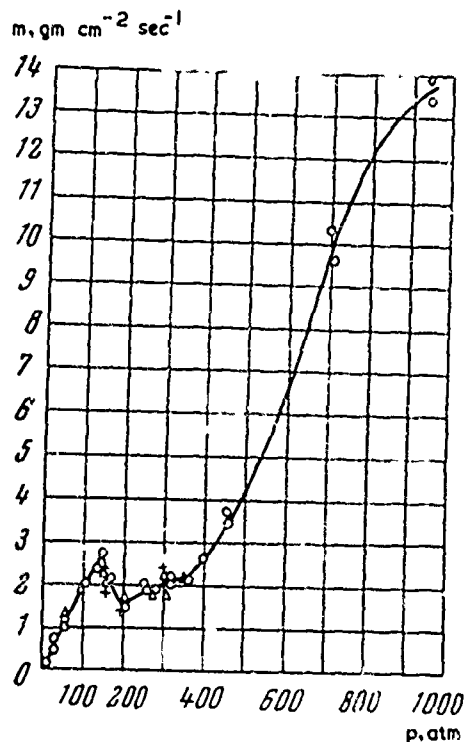


Fig. 63 Dependence $m(p)$ for pellets (diameter ϕ) of NH_4ClO_4 (not fractionated, $\delta_{\text{NH}_4\text{ClO}_4} \approx 0.99$), coated with layer of lacquer or grease:
1 - 0, $\phi = 15$ mm, layer of polyvinylchloride lacquer 0.1 mm thick
2 - 0, ϕ , but $\phi = 7$ mm
3 - +, $\phi = 7$ mm, layer of fluorinated grease

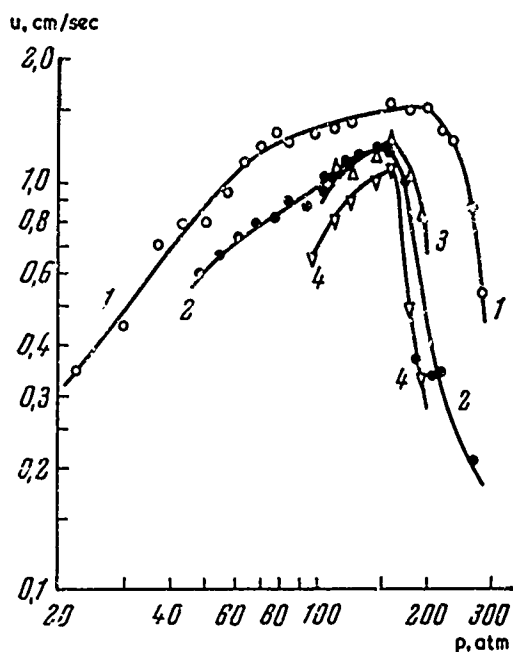
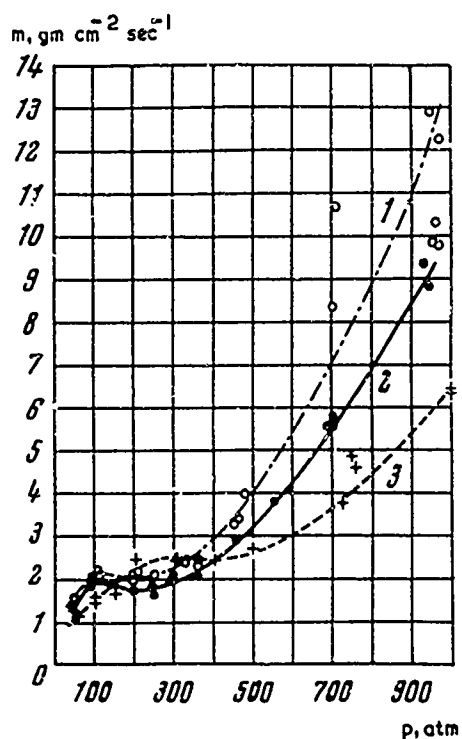


Fig. 64 Dependence $u(p)$ for uncoated pellets (4×4 mm) of NH_4ClO_4 ($\delta = 0.97-0.98$)¹²⁰
1 - non-fractionated NH_4ClO_4 , 70°C
2 - Do, 21°C
3 - $d_{\text{ox}} < 53\mu$, 21°C
4 - $d_{\text{ox}} = 74-105\mu$, 21°C

Fig. 65 Dependence $u(p)$ of NH_4ClO_4 for various particle sizes of NH_4ClO_4 (uncoated charge 8 mm dia; $\delta_{\text{NH}_4\text{ClO}_4} \approx 0.98$) (ref. 189)
1 - 3 to 7 μ 4 - 100 to 300 μ
2 - 55 to 95 μ 5 - 250 to 400 μ
3 - 5 to 250 μ 6 - 300 to 3000 μ

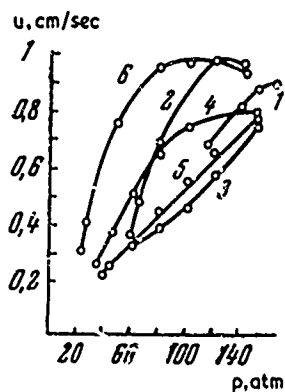


Fig. 66 Dependence of logarithm of burning rate of NH_4ClO_4 ($\sim 10\mu$) on initial temperature⁴⁷

1 - $p = 1$ atm abs, $\delta = 0.56$
2 - $p = 1$ atm abs, $\delta = 0.95$, additive 3% copper chromite
3 - As 2, but $\delta \approx 0.58$
4 - $p = 20$ atm, $\delta \approx 0.95$
5 - $p = 40$ atm, $\delta \approx 0.95$
6 - $p = 50$ atm, $\delta \approx 0.95$, additive 3% copper chromite

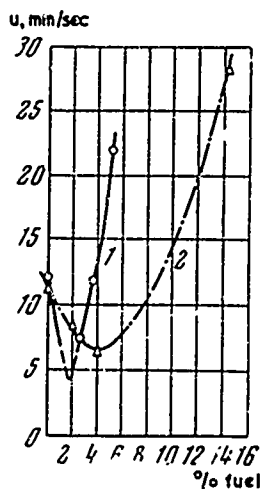
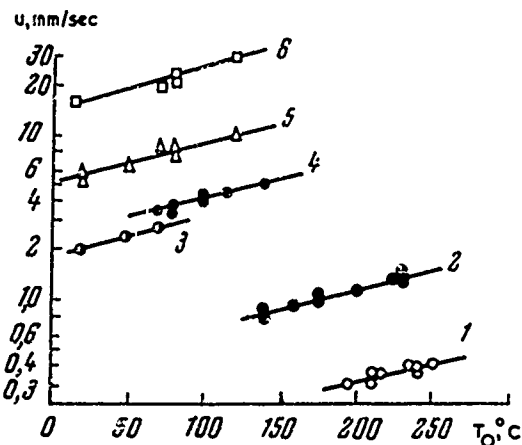


Fig. 67 Dependence of burning rate (at $p = 100$ atm) of lean mixtures of NH_4ClO_4 + fuel on percentage of fuel¹⁷³

1 - bitumen
2 - urotropine ($< 30-40\mu$)

Fig. 68 Dependence of burning rate of black powder on pressure

0 data of ref. 163
+ data of ref. 42
 ∇, Δ data of ref. 44 for two different constant pressure bombs; data over pressure range 1000-4000 atm given above on larger scale for p axis

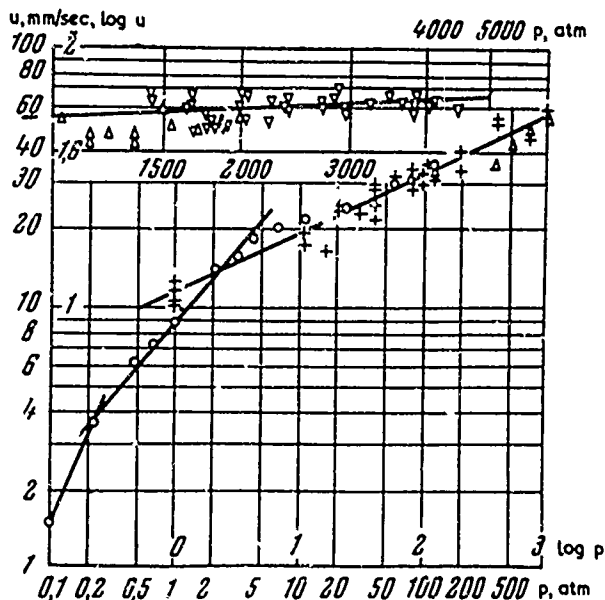


Fig. 69 Comparison of burning rate of ordinary black powder (with sulphur) and binary KNO_3 + wood charcoal mixtures¹⁶³

- 1 - ordinary black powder (data transferred from Fig. 68)
- 2 - mixture 76% KNO_3 + 24% wood charcoal
- 3 - mixture 85% KNO_3 + 15% wood charcoal

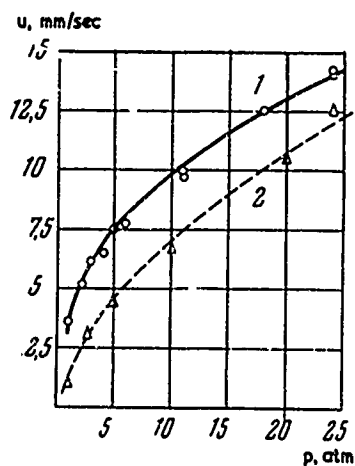
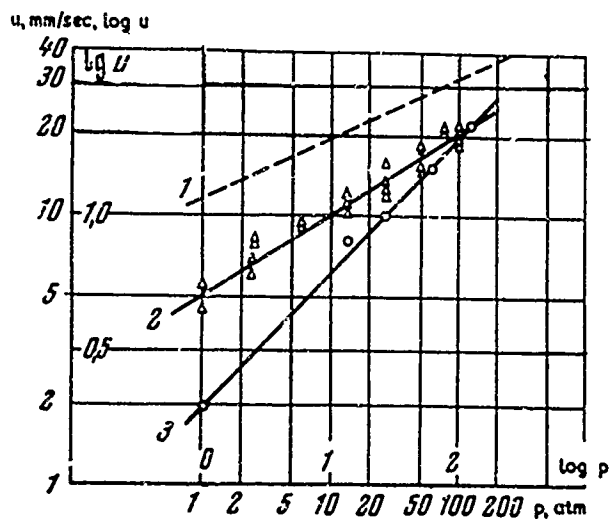


Fig. 70 Comparison of burning rates of finely divided stoichiometric mixtures of KClO_4 with (1) wood charcoal (2) bitumen¹⁶³

Fig. 71 Dependence of burning rate of finely divided KNO_3 + wood charcoal mixture on α at different pressures¹⁶³

- 1 - 50 atm
- 2 - 15 atm

